PHOTOCHEMICAL REACTIONS OF FEW SELECTED ORGANIC SYSTEMS

ABSTRACT

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

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BY

MOHD. FAISAL

DEPARTMENT OF CHEMISTRY
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2006

ABSTRACT

The thesis entitled "**Photochemical reactions of few selected organic systems**" deals with photocatalytic oxidation of few selected organic systems in aqueous suspensions of titanium dioxide under a variety of conditions with an aim to determine the optimal degradation conditions. An attempt has also been made to identify the intermediate products formed during the photooxidation process of few systems through GC/MS analysis technique in order to have a better understanding of the mechanism involved in these processes. The thesis is divided into four chapters.

The **Chapter 1** deals with photochemical reactions of four selected dye derivatives, such as coomassie blue G250 (**1**), cresol red (**2**), acridine orange (**3**) and ethidium bromide (**4**) in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique as a function of irradiation time. Irradiations were carried out in an immersion well photochemical reactor made up of pyrex glass using a 125 W medium pressure mercury lamp (radiant flux $\approx$ 2670 μWcm^{-2}). The degradation was studied using various parameters, such as type of TiO_2, solution pH, substrate concentration, catalyst concentration and in the presence of different electron acceptors besides atmospheric oxygen. In general it has been found that the degradation

curve (change in concentration vs irradiation time) of all the compounds can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. For each experiment, the degradation rate of the dye derivatives was calculated from the initial slope obtained by linear regression from the plot of the natural logarithm of the concentration of the dye derivatives as a function of irradiation time.

The degradation rate for the decomposition was calculated in terms of mole L^{-1} min^{-1} using the following equations,

$$-d[C]/dt = k\, c^n$$

C = concentration, k = rate constant, c = concentration of the pollutant, n = order of reaction

The degradation rates for the decomposition of compounds were found to be influenced by all the parameters studied. The photocatalyst, TiO_2 Hombikat UV100 was found to be slightly better for the degradation of **2**, whereas, TiO_2 Degussa P25 was found to be more efficient for the degradation of compounds **1**, **3** and **4** as compared with other TiO_2 samples. The pH of the reaction mixture has also been found to influence the degradation rate for the decomposition of compounds **1** – **4**. The different electron acceptors employed have been found to accelerate the reaction rate. The mechanistic detail and discussion regarding the effect of various

parameters on the photocatalytic degradation of different compounds under investigation has been discussed in detail.

The degradation of dye derivatives **1 - 4** was also investigated under sunlight and efficiency of degradation was compared with that of artificial light source

The **Chapter 2** of the thesis deals with the photochemical reaction of four selected pesticide derivatives, namely 2-(2,4,5-trichlorophenoxy)propionic acid (**1**), dichloroprop-P (**2**), 2,4,6-trichlorophenol (**3**) and 4-cyanophenol (**4**) in aqueous suspensions of titanium dioxide. The degradation of **1 - 4** was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique as a function of irradiation time using different parameters. The photocatalyst, Degussa P25 showed highest photocatalytic activity as compared with other TiO_2 powders for all the model compounds under investigation. The degradation rate for the decomposition of the pesticide derivatives, **1 - 3** as a function of reaction pH was found increase with the increase in pH and highest efficiency was observed at pH 10.2, 9.6 and 9.7 for compounds **1**, **2** and **3** respectively in the pH range studied. However, in case of pesticide derivative, **4** the degradation rate was found to decrease with the increase in reaction pH and highest efficiency was found at reaction pH 3. The effect of electron acceptors such as Hydrogen peroxide, potassium bromate and ammonium persulphate in addition

of atmospheric oxygen on the degradation kinetics of the model compounds, **1 - 4** was studied in the presence of Degussa P25 as photocatalyst. It could be seen that the addition of bromate ion enhanced the degradation of all the compounds markedly. Whereas the effect of electron acceptors such as H_2O_2 and persulphate ion on the degradation of compounds **1** and **3** was not pronounced. In contrasts, all the additives showed beneficial effect in the photocatalytic degradation of **2** and the addition of H_2O_2 also enhanced the degradation of **4**, markedly.

The **Chapter 3** of the thesis deals with the photochemical reactions of three selected organic systems namely 4-aminophenol (**1**), 2,4-dichloroaniline (**2**) and 4-nitroanisole (**3**) in the presence of titanium dioxide. The degradation of all the compounds was investigated by monitoring the change in substrate concentration employing UV spectroscopic analysis technique as a function of irradiation time under analogous conditions using different parameters. The degradation rates were found to be strongly influenced by the above parameters. The photocatalyst Degussa P25 was found to be more efficient for the degradation of model pollutants under investigation. Effect of substrate concentration on the degradation of the pesticide derivatives, **1 - 3** was studied at different initial concentrations of the compounds. It has been found that in the case of **1**, the rate was found to increase continuously with the increase in substrate concentration from 0.4 to

0.7 mM. Whereas, in the case of **2** the rate was found to increase with the increase in substrate concentration from 0.5 to 0.75mM and a further increase in the initial concentration of the compound lead to leveling off in the degradation rate. In contrast in the case of the compound **3**, the rate was found to increase with the increase in the initial concentration of the substrate from 0.4 to 0.8 mM and decrease in degradation rate was observed in going from 0.8 to 1.0 mM concentration of the compound. Effect of photocatalyst concentration on the degradation kinetic of model compounds, **1** - **3** under investigation was studied employing different amount of Degussa P25 varying from 0.5 to 3 gL^{-1}. It is interesting to note that in the case of compounds **1** and **3**, the rate was found to increase continuously with the increase in catalyst loading from 0.5 to 3 gL^{-1}. In contrast in the case of **2**, the rate was found to increase with the increase in catalyst loading from 0.5 to 2 gL^{-1} and a further increase in catalyst loading from 2 to 3 gL^{-1} lead to the leveling off of the rate for the decomposition of the compound

Mechanistic investigations on the primary oxidation steps related to the TiO_2-sensitized photo-oxidation of organic compounds could provide useful information about the degradation pathways involved in the decomposition of organic pollutants in waste water.

With this view, in **Chapter 4**, we have made an attempt to identify the products formed during the photooxidation of a variety of

organic compounds containing different chromophores in order to have a better understanding of the mechanism involved in the photocatalytic reactions.

The systems studied include 2, 2′- dinitrobiphenyl (**1**), N, N - dimethyl-4-nitrosoaniline (**2**), 4-(dimethylamino)benzaldehyde (**3**), phthalaldehyde (**4**) and tetramethyl-1,4-benzoquinone (**5**).

Irradiations were carried out either in H_2O or in CH_3CN/H_2O mixture in the presence of TiO_2 (Degussa P25) using 250 W high pressure mercury lamp fixed on an optical bench in a photochemical reaction vessel made of "Pyrex" glass of 250 mL capacity at different time intervals. The photocatalyst was removed through filtration and the solution was extracted with chloroform, which was subsequently dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to give a residual mass, which was analyzed by GC/MS analysis technique.

Irradiation of an aqueous suspension of 2, 2′- dinitrobiphenyl (**1**, 4 mM, 250mL) in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) for 11 h followed by work up of the reaction mixture as mentioned above. The GC/MS analysis of the chloroform extract gave a mixture of 2-hydroxy-2′-nitrobiphenyl (**6**), 2, 2′ dihydroxy biphenyl (**7**) and 2-aminobiphenyl (**11**). Irradiation of an aqueous suspension of N, N- dimethyl-4-nitrosoaniline (**2**, 4mM, 250mL) in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) for 2.5 h and the work up of reaction mixture under analogous

condition followed by GC/MS analysis of the residual mass gave rise to a mixture of N, N dimethyl-4-nitroaniline (**14**) and N, N dimethyl -1,4-benzenediamine (**15**). However, the irradiation of an aqueous suspension of 4-(dimethylamino)benzaldehyde (**3**, 4mM, 250mL) in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) for 9 h and the work up of reaction mixture under analogous condition followed by GC/MS analysis gave rise to demethylated product **17** as the only identified product. The photolysis of Phthalaldehyde (**4**, 4mM, 250mL) under identical conditions as mentioned above for 1 h and GC/MS analysis of the extract from the solution showed the formation of two products such as 1(3H)-isobenzofuranone (**23**) and 2-formyl-benzoic acid (**20**). Two products, tetramethyl hydroquinone (**34**) and 2,5-furandione-3,4-dimethyl- (**33**) have been identified on irradiation of an aqueous suspension of tetramethyl-1,4-benzoquinone (**5**, 4mM, 250mL) for 16 h in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) followed by the GC/MS analysis of the organic extract.

All the products were identified by comparing the molecular ion and mass fragmentation pattern with those reported in GC-MS library.

Reasonable mechanisms have been proposed to account for the formation of various photoproducts during the reaction of different compounds listed under Chapter **4**.

Note: The numbers of various compounds given in the parentheses corresponds to those under the respective chapters.

List of Publications

1. Photocatalysed reaction of few selected organic systems in presence of titanium dioxide,

   M. Muneer, D. Bahnemann, M. Qamar, M. A. Tariq and M. Faisal,

   Applied Catalysis A: General, 289 (**2005**) 224-230.

2. Photocatalysed degradation of two selected dyes in UV-irradiated aqueous suspensions of titania,

   M. Faisal, M. Abu Tariq and M. Muneer,

   Dyes and Pigments, (**in press**).

3. Semiconductor-mediated photocatalysed degradation of two selected azo dye derivatives, amaranth and bismarck brown in aqueous suspension,

   M. Abu Tariq, M. Faisal and M. Muneer,

   J. Hazardous Materials, B 127 (**2005**) 172-179.

4. Heterogenous photocatalysed degradation of two selected triphenylmethane dye derivatives in aqueous suspension of semiconductor,

   M. Faisal, Abu Tariq, M. Saquib and M. Muneer,

   J. Hazardous Materials, B (**Communicated**).

5. Photocatalytic degradation of two selected dye derivatives in aqueous suspension of titanium dioxide,

   M. Saquib, M. Abu Tariq, M. Faisal and M. Muneer,

   Desalination, (**Communicated**).

6. Heterogeneous photocatalysed reactions of three selected organic systems in aqueous suspension of titanium dioxide,

M. Faisal, M. Abu Tariq and M. Muneer

Research on Chemical Intermediates, (**under preparation**).

7. Titanium dioxide mediated photocatalysed degradation of two selected pesticide derivatives,

   M. Faisal, M. Abu Tariq and M. Muneer,

   Journal of Environmental Management, (**under preparation**).

Paper presented/accepted in conferences

8. Photocatalysed degradation of two selected dyes in UV-irradiated aqueous suspension of titania,

   M. Faisal, M. Abu Tariq and M. Muneer,

   National Conference on Recent Trends in Surface Chemistry (RTSC-05), on 13-14th March 2005, Department of Chemistry, Guru Jambheshwar University, Hisar-125 001, Haryana, India (**oral presentation**).

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DEDICATED TO MY PARENTS

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Dated.....

CERTIFICATE

Certified that the work embodied in this thesis entitled "**Photochemical reactions of few selected organic systems**" has been carried out by **MOHD. FAISAL** under my supervision and same has not been submitted for a degree elsewhere.

M. Muneer

(M. Muneer)

CONTENTS

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Aligarh Muslim University, Aligarh, India under the supervision of ***Prof. M. Muneer.***

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

Mohd Faisal

(Mohd Faisal)

ACKNOWLEDGEMENTS

Praise be to ALLAH, the Lord of the worlds, Who says in His Glorious book, "Iqra! (or Read!) in the name of thy Lord and Cherisher, Who has created (all that exists), Who has taught (the use of) the pen." And peace and blessing of ALLAH (SWT) be upon the noblest of the Prophets and Messengers, our beloved Prophet Mohammad (SAW) who said, "Seek knowledge from cradle to grave." I praise You ALLAH (SWT) for everything You bestowed upon me, especially for Your favour in completing this work.

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(MOHD FAISAL)

PREFACE

The thesis entitled "**Photochemical reactions of few selected organic systems**" deals with photocatalytic oxidation of few selected organic systems in aqueous suspensions of titanium dioxide under a variety of conditions with an aim to determine the optimal degradation conditions. An attempt has also been made to identify the intermediate products formed during the photooxidation process of few systems through GC/MS analysis technique in order to have a better understanding of the mechanism involved in these processes. The thesis is divided into four chapters.

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The **Chapter 3** of the thesis deals with the photochemical reactions of three selected organic systems namely 4-aminophenol (**1**), 2,4-dichloroaniline (**2**) and 4-nitroanisole (**3**) in the presence of titanium dioxide. The degradation of all the compounds was investigated by monitoring the change in substrate concentration employing UV spectroscopic analysis technique as a function of irradiation time under analogous conditions using different parameters. The degradation rates were found to be strongly influenced by the above parameters. The photocatalyst Degussa P25 was found to be more efficient for the degradation of model pollutants under investigation. Effect of substrate concentration on the degradation of the pesticide derivatives, **1** - **3** was studied at different initial concentrations of the compounds. It has been found that in the case of **1**, the rate was found to increase continuously with the increase in substrate concentration from 0.4 to

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With this view, in **Chapter 4**, we have made an attempt to identify the products formed during the photooxidation of a variety of

organic compounds containing different chromophores in order to have a better understanding of the mechanism involved in the photocatalytic reactions.

The systems studied include 2, 2′- dinitrobiphenyl (**1**), N, N - dimethyl-4-nitrosoaniline (**2**), 4-(dimethylamino)benzaldehyde (**3**), phthalaldehyde (**4**) and tetramethyl-1,4-benzoquinone (**5**).

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All the products were identified by comparing the molecular ion and mass fragmentation pattern with those reported in GC-MS library.

Reasonable mechanisms have been proposed to account for the formation of various photoproducts during the reaction of different compounds listed under Chapter **4**.

Note: The numbers of various compounds given in the parentheses corresponds to those under the respective chapters.

Chapter 1

PHOTOCHEMICAL REACTIONS OF FOUR SELECTED DYE DERIVATIVES, COOMASSIE BLUE G250, CRESOL RED, ACRIDINE ORANGE AND ETHIDIUM BROMIDE IN AQUEOUS SUSPENSIONS OF TITANIUM DIOXIDE[1-2]

1.1 Abstract

The photochemical reactions of four selected dye derivatives, such as coomassie blue G250 (**1**), cresol red (**2**), acridine orange (**3**) and ethidium bromide (**4**) have been investigated in aqueous suspensions of titanium dioxide (TiO_2) under a variety of conditions. The reaction was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique as a function of irradiation time. All the dyes under investigation were found to degrade when irradiated in the presence of TiO_2. The degradation was studied under different conditions such as different types of TiO_2, reaction pH, catalyst and substrate concentration, and in the presence of electron acceptors like H_2O_2, $(NH_4)_2S_2O_8$, and $KBrO_3$ besides atmospheric oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The degradation of all the dyes were also investigated under sunlight and the efficiency of degradation was compared with that of the artificial light source. The photocatalyst Degussa P25 was found to be more efficient for the

degradation of all the dyes except cresol red (**2**), where Hombikat UV 100 was better.

1.2 Introduction

Water is one of the most abundantly available substances in nature. It is an important constituent of all forms of life and form 75% of the matter of the earth crust which is distributed in nature in different forms such as ground water, surface water etc. The amount of water used for commercial (industrial) and municipal (domestic) purposes is much higher as compared to water used for drinking purpose per year all over the world. This shows that even a small shortage of water can become a threat to mankind especially in developing countries. The water present on earth is contaminated through various sources such as industrial effluents, agricultural runoff and chemical spills[3]. These effluents contain a variety of non-biodegradable substances that are toxic in nature. One principal source of water pollution is dye-based industries where wastewater is colored due to the presence of dyes. Recent studies show that over $7X10^5$ tones of dyes are produced annually worldwide and approximately 1-15% of these dyes are lost[4] during manufacturing and processing operations of which 20% of the resultant color enters the environment through effluents from industrial wastewater treatment plants, which pose a major problem for the industries as well as a threat to the environment[5-9]. This polluted colored water is of no use, neither for irrigation nor for domestic

purposes. The removal of color from colored wastewater has been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but often due to their visibility in receiving waters.

Decolourization of dye effluents has therefore acquired increasing attention. Development of appropriate methods for the degradation of contaminated drinking, ground, surface and wastewaters containing toxic or nonbiodegradable compounds is necessary. Among these methods photocatalytic processes involving TiO_2 semiconductor particles under UV light illumination has shown to be potentially advantageous and useful in the treatment of wastewater pollutants[10-13]. Earlier studies have shown that a wide range of organic substrates such as alkanes, alkenes, aromatics, surfactants, herbicides, pesticides, fungicides and insecticides can be completely decomposed in the presence of TiO_2 and oxygen[14-17].

1.2.1 Mechanism of heterogeneous photocatalysis

Heterogeneous photocatalysis is a process in which two active phases solid and liquid are present .The solid phase is a catalyst, usually a semiconductor. The molecular orbital of semiconductors have a band structure. The bands of interest in photocatalysis are the populated valence band (VB) and its largely vacant conduction band (CB),[18] which is commonly characterized by band gap energy (E_{bg}). The semiconductors may be photoexcited to form electron-donor sites

(reducing sites) and electron-acceptor sites (oxidising sites), providing great scope for redox reaction. When the semiconductor is illuminated with light ($h\nu$) of energy greater than that of the band gap, an electron is promoted from the VB to the CB leaving a positive hole in the valence band and an electron in the conduction band as illustrated in Fig. **1.1**.

If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h^+_{vb} may react with surface-bound H_2O or OH^- to produce the hydroxyl radical and e^-_{cb} is picked up by oxygen to generate superoxide radical anion (O_2^-), as indicated in the following equations 1-3;

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \quad [1]$$

$$O_2 + e^-_{cb} \rightarrow O^{\bullet -}_2 \quad [2]$$

$$H_2O + h^+_{vb} \rightarrow {}^{\bullet}OH + H^+ \quad [3]$$

It has been suggested that the hydroxyl radical ($^{\bullet}OH$) and superoxide radical anion ($O_2^{\bullet -}$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the degradation of the pollutants.

Among the semiconductors, TiO_2 has proven to be the most suitable for widespread environmental applications. Titanium dioxide is biologically and chemically inert; it is stable to photo and chemical

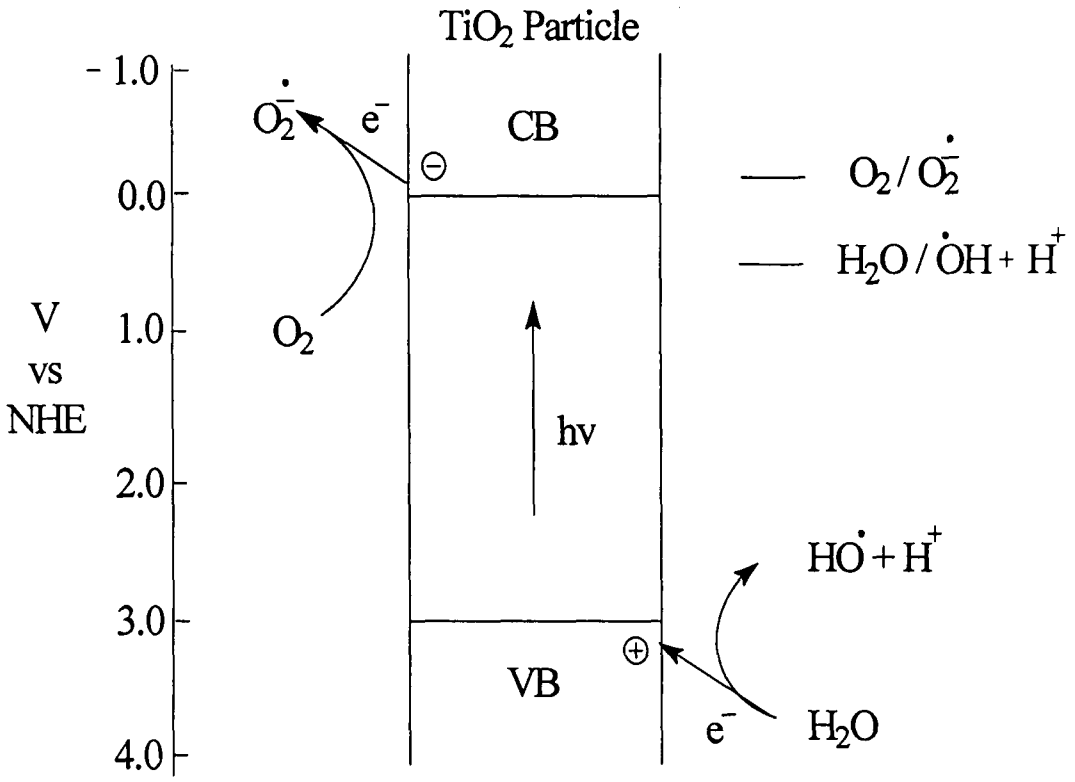

TiO2 Particle
- 1.0
0.0
1.0
2.0
3.0
4.0
V
vs
NHE
O2-
e-
CB
O2
hv
VB
e-
H2O
HO + H+
O2 / O2-
H2O / OH + H+

Figure 1.1

corrosion, and inexpensive. It also shows the resistivity against strong acids and bases and its stability under illumination.[19] Furthermore, TiO_2 is of special interest since it can use natural (solar) UV radiation. This is because TiO_2 has an appropriate energetic separation between its valence and conduction bands, which can be surpassed by the energy of a solar photon. The VB and CB energies of the TiO_2 are estimated to be +3.1 and -0.1 volts, respectively, which means that its band gap energy is 3.2 eV and therefore absorbs in the near UV light (λ<387 nm). Many organic compounds have a potential above that of the TiO_2 valence band and therefore can be oxidized. In contrast, fewer organic compounds can be reduced since a smaller number of them have a potential below that of the TiO_2 conduction band.[20] Although ZnO seems to be a suitable alternative to TiO_2, it dissolves in acidic solutions and can therefore not be used for technical applications.[21] Other semiconductor particles (e.g., CdS or GaP) absorb larger fractions of the solar spectrum than TiO_2 and can form chemically activated surface-bond intermediates, but unfortunately, such catalysts are degraded during the repeated catalytic cycles usually involved in heterogeneous photocatalysis.

For oxidation reactions to occur, the VB must have a higher oxidation potential than the material under consideration. The redox potential of the VB and the CB for different semiconductors varies between +4.0 and -1.5 volts versus Normal Hydrogen Electrode (NHE)

respectively. Therefore, by careful selection of the semiconductor photocatalyst, a wide range of species can be treated via these processes.

In the case of dyes direct absorption of light can lead to charge injection from the excited state of the dye to the conduction band of the semiconductor as summarized in the following equations 4-5;

$$Dye_{ads} + hv \rightarrow Dye_{ads}^{*} \quad [4]$$

$$Dye_{ads}^{*} + TiO_2 \rightarrow Dye_{ads}^{+\bullet} + TiO_2(e^-) \quad [5]$$

There are several classes of dyes, which do not favour donation of electrons from the excited states, such as anthraquinone dyes because of the presence of two electron-withdrawing carbonyl groups, which are susceptible to accept an electron rather than donate an electron.

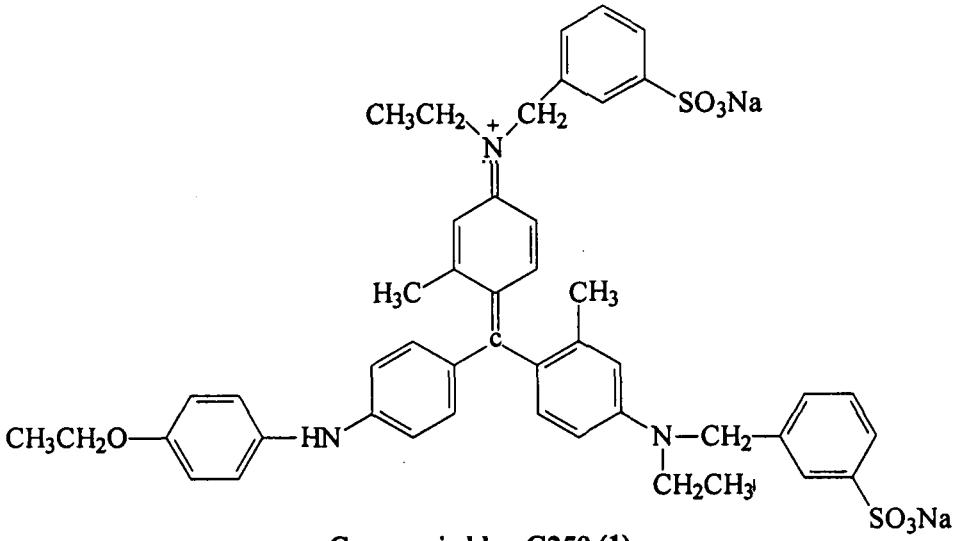
Triphenyl methane dyes are extensively used in textile industry, paper industry, as a biological stain[22-24] and as a dermatological agent[25,26] . Acridine orange and ethidium bromide are mainly used in cytochemical staining[27-32]. Earlier studies[33-45] have shown that heterogenous photocatalytic oxidation processes can be used for removing colouring material from dye effluent in the presence of light. A few studies relating the degradation of triphenylmethane dye derivatives in the presence of TiO_2 has been reported earlier from our laboratory as well as by others[46-49]. To best of our knowledge there is

no report on the photocatalytic degradation of acridine orange and ethidium bromide. Our investigations on the degradation of dyes indicate that the parameters (like reaction pH, type of TiO_2 ,substrate concentration, catalyst concentration) influencing the degradation depends on the chromophores and substituent present on them. With this view, we have studied the degradation of four selected dye derivatives, such as coomassie blue G250 (**1**), cresol red (**2**), acridine orange (**3**) and ethidium bromide (**4**) shown in Chart **1.1**, in aqueous suspensions of TiO_2 under a variety of conditions with an aim to determine the optimal degradation condition .

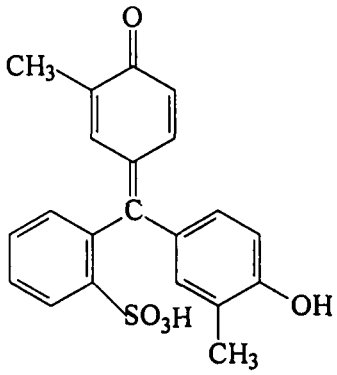
1.3 Experimental

1.3.1 Reagents and chemicals

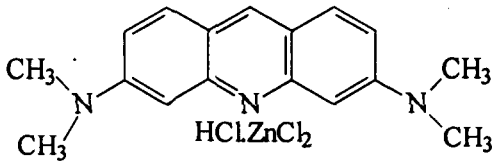
The dye derivatives coomassie blue G250 (**1**), cresol red (**2**), acridine orange (**3**) and ethidium bromide (**4**) were obtained from Polysciences, Inc., Warrington, USA, SD fine chemical limited India, otto kemi, Bombay, India and Sigma -Aldrich. They were used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst titanium dioxide, Degussa P25 (Degussa AG),[50] was used in most of the experiments, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH)[51] and PC500 (Milenium inorganic chemicals),[51] were used for comparative studies. Degussa P25 consist of 75% anatase and 25% rutile with a specific BET-surface area of 50 m^2g^{-1} and primary particle



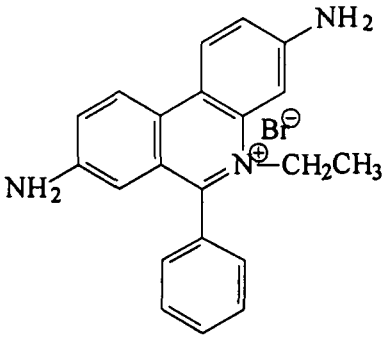
Coomassie blue G250 (1)



Cresol red (2)



Acridine orange (3)



Ethidium bromide (4)

Chart 1.1: Chemical structure and name

size of 20 nm.[52] Hombikat UV100 consist of 100% anatase with a specific BET-surface area >250 m^2g^{-1} and primary particle size of 5 nm.[53] The photocatalyst PC500 has a BET-surface area of 287 m^2g^{-1} with 100% anatase and primary particle size of 5-10 nm.[54] The other chemical used in this study such as NaOH, HNO_3, $(NH_4)_2S_2O_8$, H_2O_2 and $KBrO_3$ were obtained from Merck.

1.3.2 Procedure

Stock solution of the dye derivatives containing desired concentrations were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of atmospheric oxygen was used. A simplified diagram of the reactor system is shown in Fig. **1.2**.

For irradiation experiment, 250 mL aqueous solution of the dye with desired concentration was taken into the photoreactor and required amount of photocatalyst was added. The solution was stirred and bubbled with atmospheric oxygen for at least 15 minutes in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with atmospheric oxygen throughout each experiment.

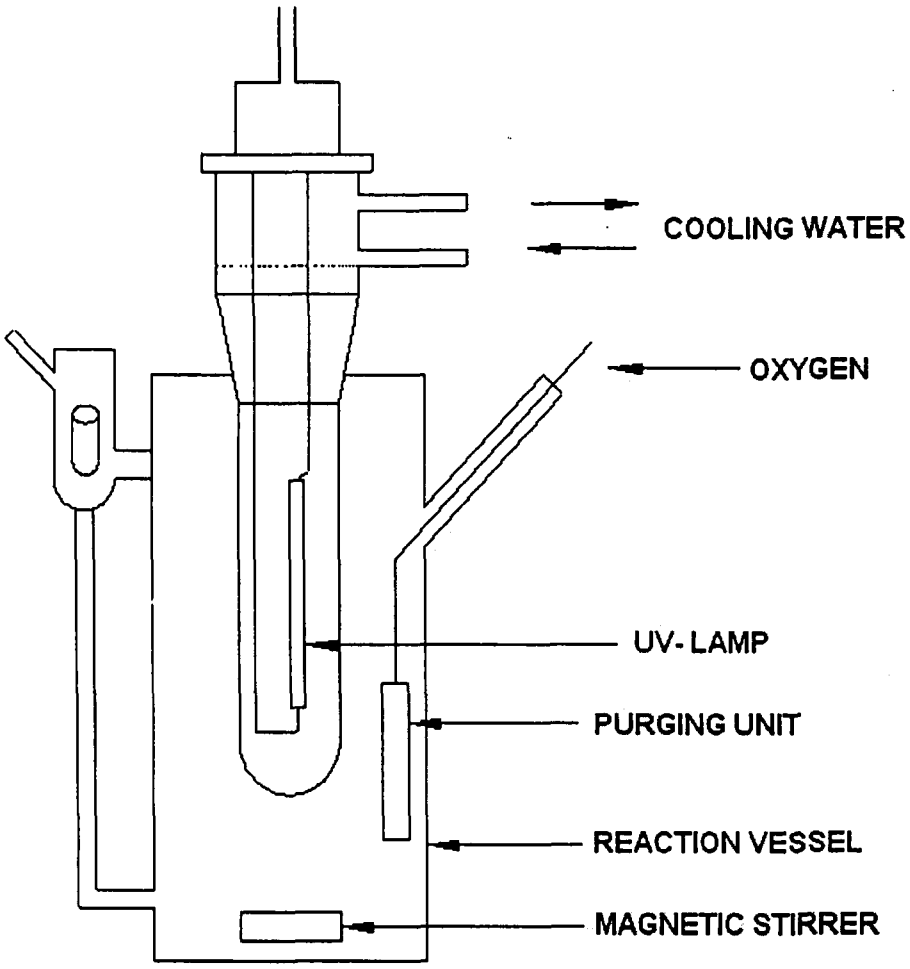

COOLING WATER
OXYGEN
UV- LAMP
PURGING UNIT
REACTION VESSEL
MAGNETIC STIRRER

Figure 1.2

Irradiations were carried out using a 125 W medium pressure mercury lamp (radiant flux ≈ 2670 μWcm^{-2}).

IR-radiation and short-wavelength UV-radiation were eliminated by water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during irradiation and analyzed after centrifugation.

The sunlight experiments were carried out in order to compare the degradation efficiency of the compound under investigation with that of artificial light source. Reactions were carried out in the same photochemical reaction vessel where irradiations were carried out using the artificial light source. Aqueous solution (250 mL) of desired concentration of the model compound containing required amount of photocatalyst was taken into the reaction vessel and stirred for 15 min in the dark and the solution was then placed on flat platform under sunlight with continuous stirring and purging of atmospheric oxygen. Samples (10 mL) were collected before and at regular intervals during the illumination and analyzed after centrifugation.

1.3.3 Analysis

1.3.3.1 Photodegradation of the dye derivatives

The photodegradation of the dye was monitored using UV spectroscopic analysis technique (Shimadzu UV-Vis 1601). The double beam spectrophotometer has an in-built tungsten and

deuterium lamps, which provide the measurement of optical density (OD) in the range 200-1100 nm (near UV and visible regions). The samples were analyzed using quartz cuvette, as it has zero absorption in the above wavelength regions.

The concentrations of dye derivatives were calculated by standard calibration curve obtained from the absorbance of the dyes at different concentrations. The degradation of the compounds, **1 - 4** was followed by measuring the absorbance at their λmax as a function of irradiation time.

1.4 Results and Discussion

1.4.1 Photocatalysis of aqueous suspensions of dye derivatives, 1 - 4 in the presence of TiO_2

Irradiation of an aqueous suspension of the dye derivatives, **1 - 4** in the presence of TiO_2 (Degussa P25, $1gL^{-1}$) with a "Pyrex" filtered output of a 125 W medium pressure mercury lamp with constant bubbling of atmospheric oxygen lead to decrease in absorption intensity as a function of time. This absorption intensity is used to calculate the concentration by standard calibration curve obtained from the absorption intensity of the dye derivatives at different concentration. Figs. **1.3-1.6** show the change in concentration as a function of time on irradiation of an aqueous suspensions of dye derivatives, **1 - 4** in the presence and absence of photocatalyst. It could be seen from the figure that all the dyes undergo degradation

when irradiated in the presence of TiO_2, whereas no observable loss of dye takes place in the absence of TiO_2.

The curve for the change in substrate concentration as a function of irradiation time for the dye derivatives, **1 - 3** as shown in Figs.**1.3 - 1.5** can be fitted reasonably well by exponential decay curve suggesting first order kinetics. In contrast the curve showing the change in concentration vs irradiation time for the photocatalytic degradation of the dye derivative, **4** can be fitted reasonably well by a zero order reaction. For the sake of uniformity, we have considered this curve also as a first order kinetics. As a representative example, Fig. **1.7** shows the linear regression curve fit for the natural logarithm of the concentration vs. irradiation time for the degradation of acridine orange (**3**). For each experiment, the degradation rate constant of the dye derivative was calculated from the plot of the natural logarithm of concentration of the dye derivative as a function of irradiation time. The degradation rate for the decomposition of the dye was calculated using formula given below;

$$-d[C]/ dt = kc^n \qquad [6]$$

C = concentration of the pollutant, k = rate constant, c = concentration, n = order of reaction.

The degradation rate for the decomposition of dye for the first order reaction was calculated in terms of mol L^{-1} min^{-1}.

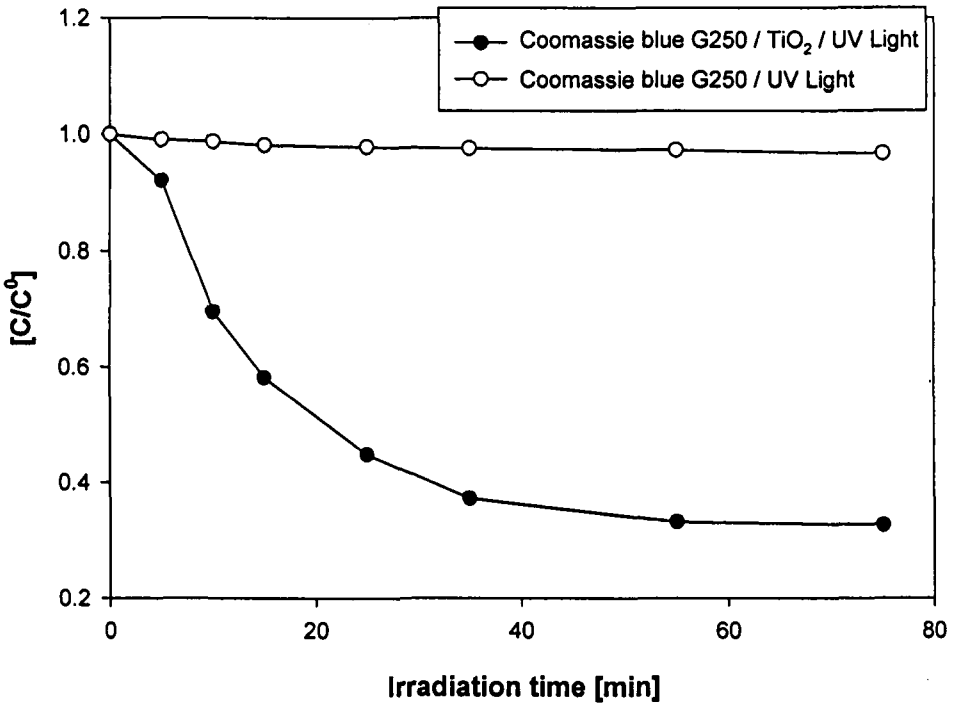


Figure 1.3. Change in concentration as a function of time for irradiation of an aqueous suspension of coomassie blue G250 (1) in the presence and absence of the photocatalyst. Experimental conditions: 0.5 mM coomassie blue G250, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 582 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 75 min.

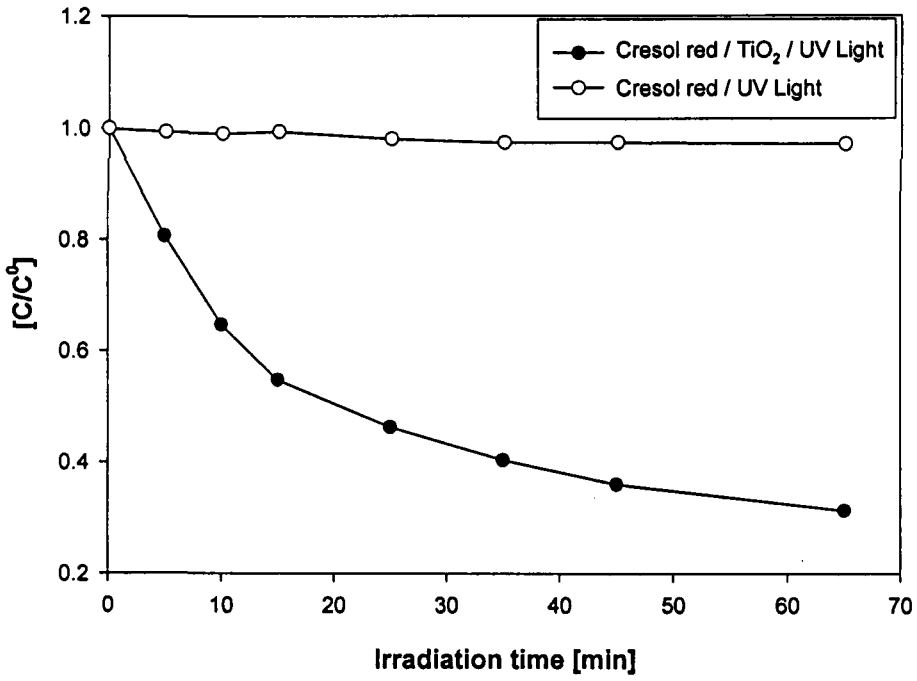


Figure 1.4. Change in concentration as a function of time for irradiation of an aqueous suspension of cresol red (**2**) in the presence and absence of the photocatalyst.

Experimental conditions: 0.3 mM cresol red, V=250 mL, photocatalyst: TiO_2 (Hombikat UV100, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 436 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 65 min.

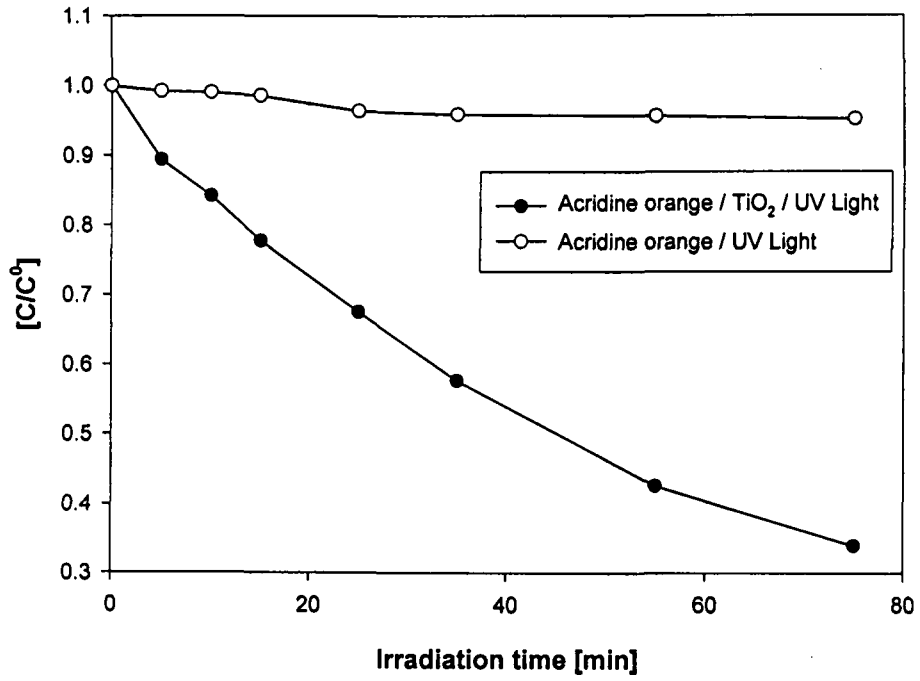


Figure 1.5. Change in concentration as a function of time for irradiation of an aqueous suspension of acridine orange (3) in the presence and absence of the photocatalyst.

Experimental conditions: 0.4 mM acridine orange, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 449 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 75 min.

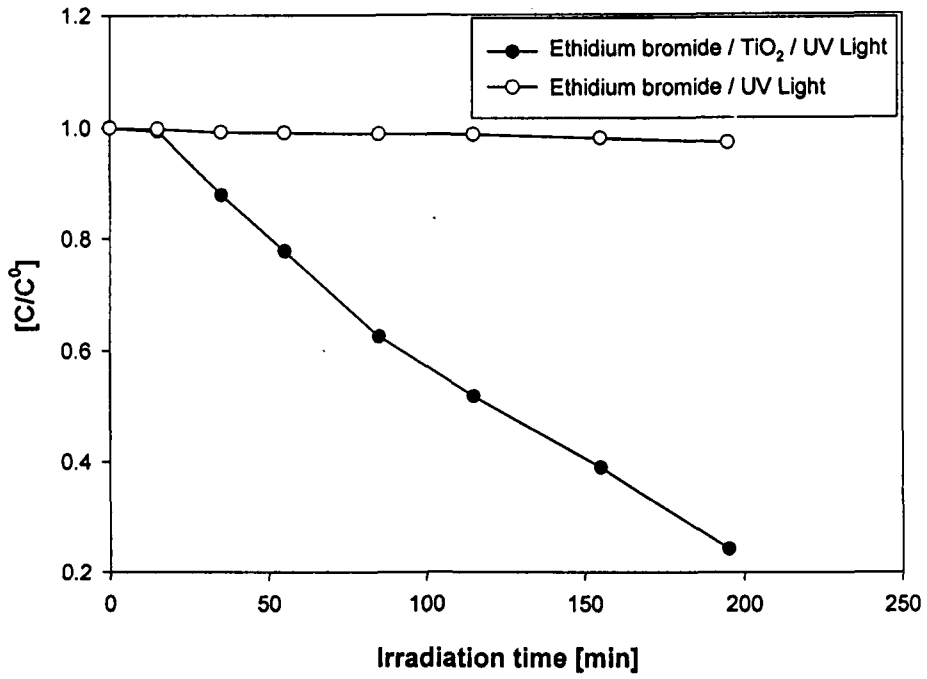


Figure 1.6. Change in concentration as a function of time for irradiation of an aqueous suspension of ethidium bromide (4) in the presence and absence of the photocatalyst.
Experimental conditions: 0.2 mM ethidium bromide, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 482 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 195 min.

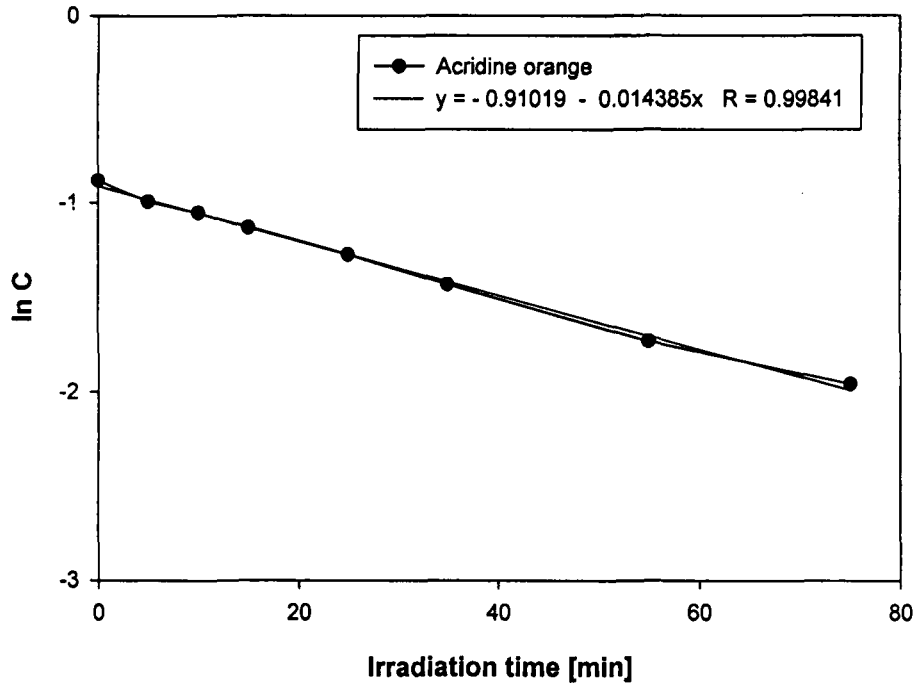


Figure 1.7. Plot showing the linear regression curve fit for the natural logarithm of concentration of acridine orange(**3**) as a function of irradiation time.

Control experiments were carried out in all cases by irradiating the aqueous solution of the dye in the absence of photocatalyst, where no observable loss of the dye was observed. The zero irradiation time reading was obtained from the blank solution kept in the dark, but otherwise treated similarly to the irradiated solution.

1.4.2 Comparison of different types of photocatalyst at varying concentration

We have tested the photocatalytic activity of three different commercially available TiO_2 (namely Degussa P25, Hombikat UV100 and Millennium Inorganic PC500) employing varying catalyst concentrations on the degradation kinetics of the dye derivatives under investigation. The degradation rate obtained for the decomposition of **1 - 4**, in the presence of different types of TiO_2 at varying catalyst loading is shown in Figs. **1.8 - 1.11**, respectively. It has been observed that the degradation of dye derivatives, **1**, **3** and **4** under investigation proceed rapidly in the presence of Degussa P25 as compared with other TiO_2 samples. Whereas, the photocatalyst, Hombikat UV100 showed better photocatalytic activity for the degradation of dye derivative **2**. It is interesting to note that the degradation rate for the decomposition of dye derivative **1** was found to increase with the increase in catalyst concentration from 0.5 to 3 gL^{-1} when photocatalysts such as Degussa P25 and Hombikat UV100 were used as shown in Fig. **1.8**. In contrast, when photocatalyst such as PC-500 was used the rate increases with the increase in catalyst loading from

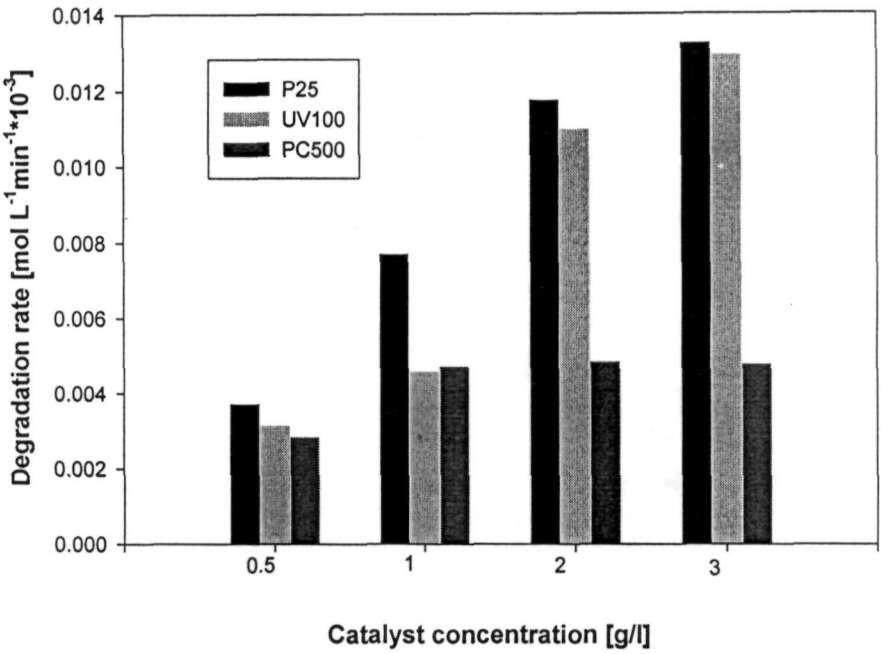


Figure 1.8. comparision of degradation rate of the decomposition of coomassie blue G250 (**1**) in the presence of different types of catalyst at different catalyst concentartions.

Experimental conditions: 0.5 mM coomassie blue G250, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV 100 and PC 500 (0.5, 1, 2 and 3 gL^{-1}), irradiation time = 75 min.

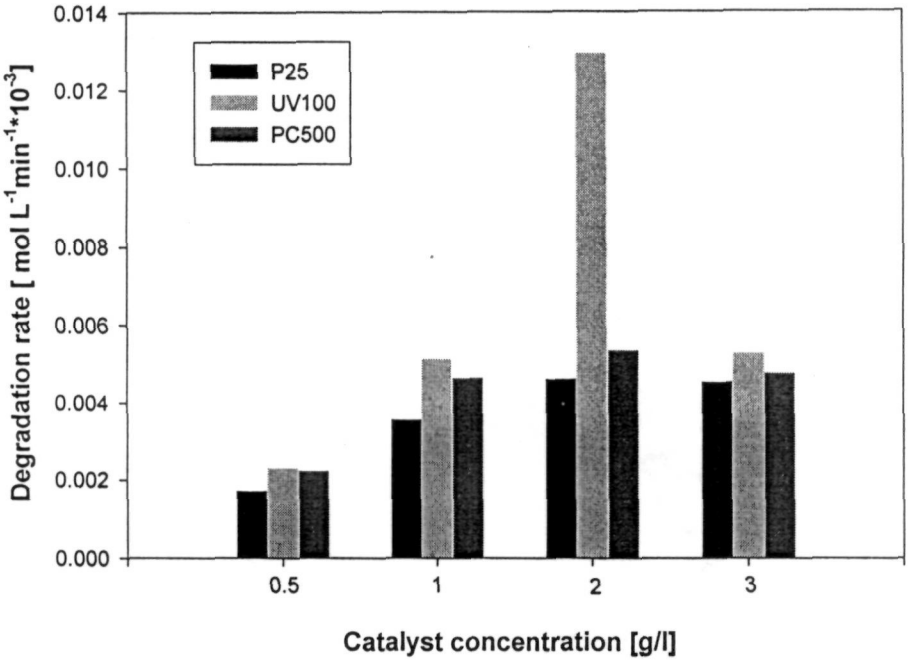


Figure 1.9. Comparison of degradation rate for the decomposition of cresol red (**2**) in the presence of different types of photocatalyst at different concentrations.
Experimental conditions: 0.3 mM cresol red, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC 500 (0.5, 1, 2 and 3 gL^{-1}), irradiation time = 65 min.

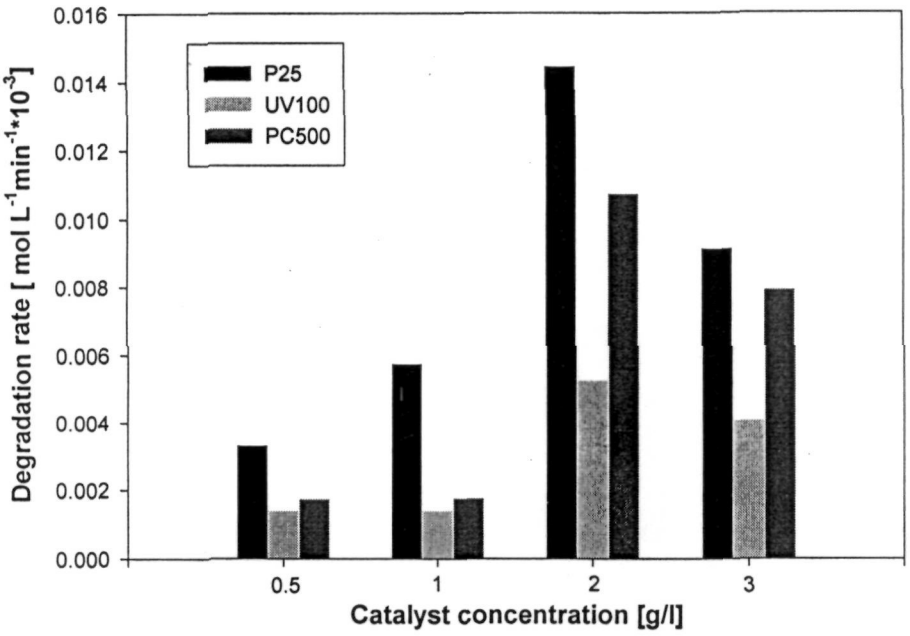


Figure 1.10. Comparison of degradation rate for decomposition of acridine orange (**3**) in the presence of different types of photocatalyst at different catalyst concentrations.
Experimental conditions: 0.4 mM acridine orange, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC 500 (0.5, 1, 2 and 3 gL^{-1}), irradiation time = 75 min.

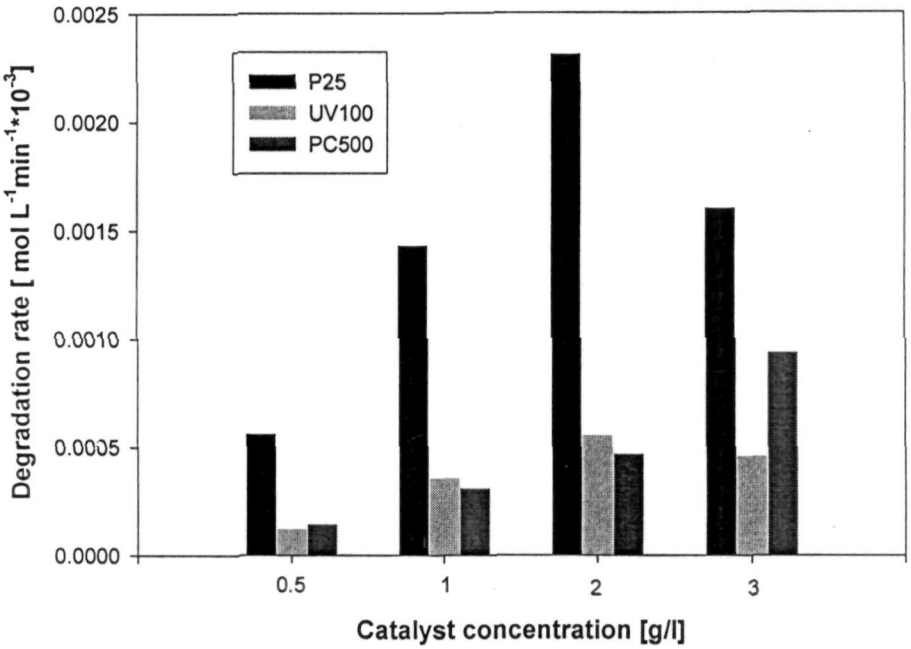


Figure 1.11. Comparison of degradation rate for decomposition of ethidium bromide (**4**) in the presence of different types of photocatalyst at different catalyst concentrations.

Experimental conditions: 0.2 mM ethidium bromide, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC 500 (0.5, 1, 2 and 3 gL^{-1}), irradiation time = 195 min.

0.5 to 1 gL^{-1} and remain constant upto 3 gL^{-1}. On the other hand in the case of compounds **2**, **3** and **4** the rate was found to increase with the increase in catalyst concentration from 0.5 to 2 gL^{-1} and further increase in catalyst concentration lead to decrease in the degradation rate when photocatalysts such as Hombikat UV 100 and Degussa P25 were used.

Martin et al.[55] has shown that Degussa P25 owes its high photoreactivity due to slow recombination between electron and holes whereas Sachtleben Hombikat UV100 has a high photoreactivity due to fast interfacial electron transfer rate. Since the photocatalyst Degussa P25 was found to be more efficient photocatalyst for the degradation of dye derivatives **1**, **3** and **4**, it indicates that the rate-limiting step is the lifetime of electron hole pairs, whereas in case of dye derivative, **2** (in the presence of Hombikat UV100) the reaction could be proceeding via interfacial electron transfer reaction.

Earlier studies have shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds.[56-58] On the other hand Lindner et al.[59] showed that Hombikat UV100 was almost four times more effective than Degussa P25 when dichloroacetic acid was used as the model pollutant. Also Hombikat UV100 was found to be better for the degradation of benzidine, 1,2-diphenyl hydrazine[60] and remazol brilliant blue R[27] as shown in a recent study. These results indicate

that the activity of the photocatalyst also depends on the type of the model pollutant.

The reason for the better photocatalytic activity of Degussa P25, could be attributed to the fact that Degussa P25 being composed of small nano-crystallites of rutile being dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron-hole pairs. The electron transfer, from the rutile conduction band to electron traps in anatase phase takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react.[61]

Whether in static, slurry, or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However, it was observed that above a certain concentration, the reaction rate decreases and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of TiO_2 in which all the particles, i.e., surface exposed, are totally illuminated. When the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration $[(TiO_2)_{OPT}]$ has to be found, in order to avoid excess catalyst and insure total absorption of efficient photons.

In the following experiments, Degussa P25 was used as the photocatalyst for the degradation of dye derivatives **1**, **3** and **4** and Hombikat UV 100 for degradation of dye derivative **2**, since these materials exhibited the highest overall activity for the degradation of compounds as compared with other TiO_2 powders.

1.4.3 pH Effect

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. Employing Degussa P25 as photocatalyst the decomposition of dye derivatives, **1 - 4** in the aqueous suspensions of TiO_2 was studied in the pH range between 2-10. The pH of the reaction mixture was adjusted at the start of irradiation by adding aqueous solution of HNO_3 or NaOH. A decrease in pH of reaction mixture was observed at the end of irradiation. Figs. **1.12 - 1.15** show the degradation rate for the decomposition of the dye derivatives **1- 4**, as a function of reaction pH.

The degradation rate for the decomposition of the dye derivative, **1** was found to increase with increase in pH from 4.25 to 8.1 and further increase in pH lead to slight decrease in degradation rate. However, in case of **2** (where the effect of pH on the degradation rate was studied at three different pH values such as 2, 3.5 and 5.5) the rate was found to decrease with the increase in reaction pH and

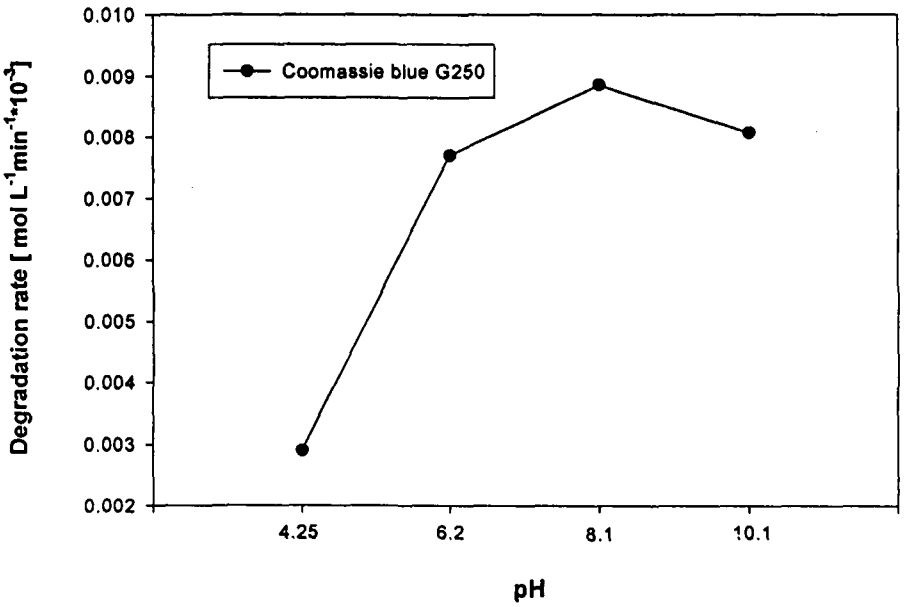


Figure 1.12. Influence of pH on the degradation rate for the decomposition of coomassie blue G250 (1).
Experimental conditions: 0.5 mM coomassie blue G250, V=250 mL, photocatalyst : TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (4.25, 6.2, 8.1, and 10.1), irradiation time = 75 min.

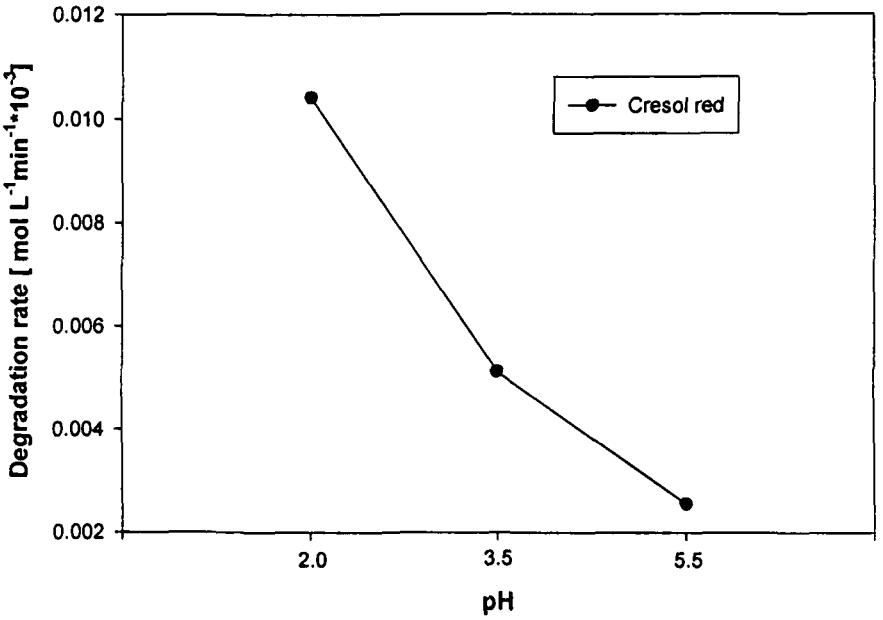


Figure 1.13. Influence of pH on the degradation rate for the decomposition of cresol red (**2**).

Experimental conditions: 0.3 mM cresol red, V=250 mL, photocatalyst : TiO_2 (Hombikat UV100, 1 gL^{-1}), reaction pH (2.0, 3.5 and 5.5), irradiation time = 65 min.

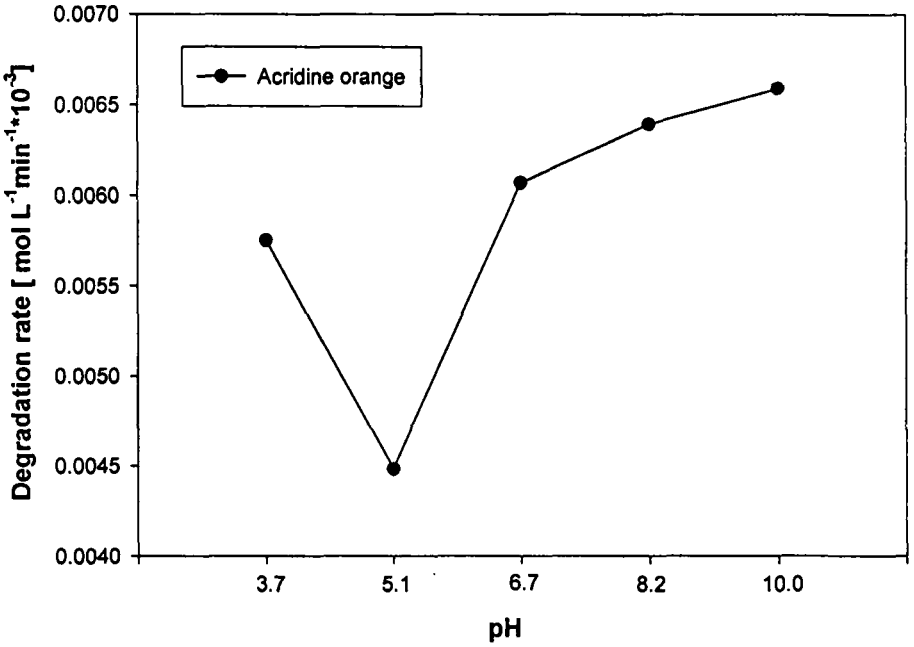


Figure 1.14. Influence of pH on the degradation rate for the decomposition of acridine orange (**3**).

Experimental conditions: 0.3 mM acridine orange, V=250 mL, photocatalyst : TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (3.7, 5.1, 6.7, 8.2 and 10.0), irradiation time = 75 min.

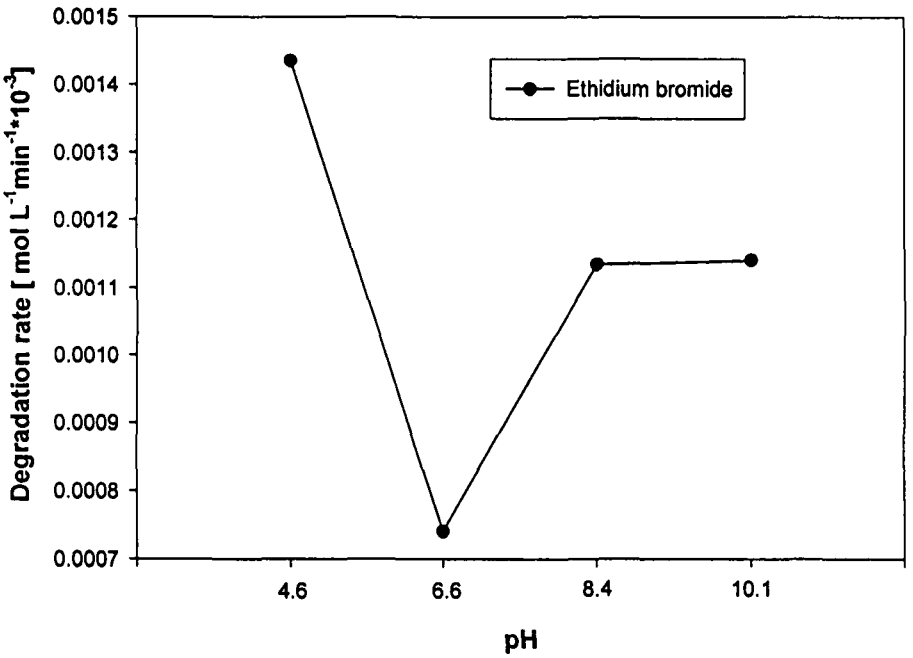


Figure 1.15. Influence of pH on the degradation rate for the decomposition of ethidium bromide (4).
Experimental conditions: 0.2 mM ethidium bromide, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (4.6, 6.6, 8.4 and 10.1), irradiation time = 195 min.

highest efficiency was observed at pH 2. The degradation of this particular dye could not be studied at higher pH values because of change in color and shift in λ_{max}. Whereas in the case of dye derivative **3**, the degradation rate for the decomposition was found to decrease from pH 3.7 to 5.1 and further increase in pH lead to increase in the degradation rate. A similar trend was observed in the photocatalytic degradation of dye derivative, **4** as a function of pH.

The adsorption of dye derivatives, **1 – 4** on the surface of the photocatalyst was investigated by stirring the aqueous solution of the dye in the dark for 24 h at different pH values using 1 gL^{-1} of catalyst. Analysis of the sample after centrifugation indicate no observable loss of the compound in the case of dye derivative **4** in the pH range from 3.1 to 10. However, in the case of dye derivatives, **1, 2** and **3** some observable loss of the compound was seen at pH 4.25 (in case of **1**) at pH 2.0 (in case of **2**) and at pH 10.0 (in the case of dye **3**) as shown in Fig. **1.16**, **1.17** and **1.18** respectively.

The interpretation of pH effect on the photocatalytic process is very difficult because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process. The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions respectively, as shown in following equations,

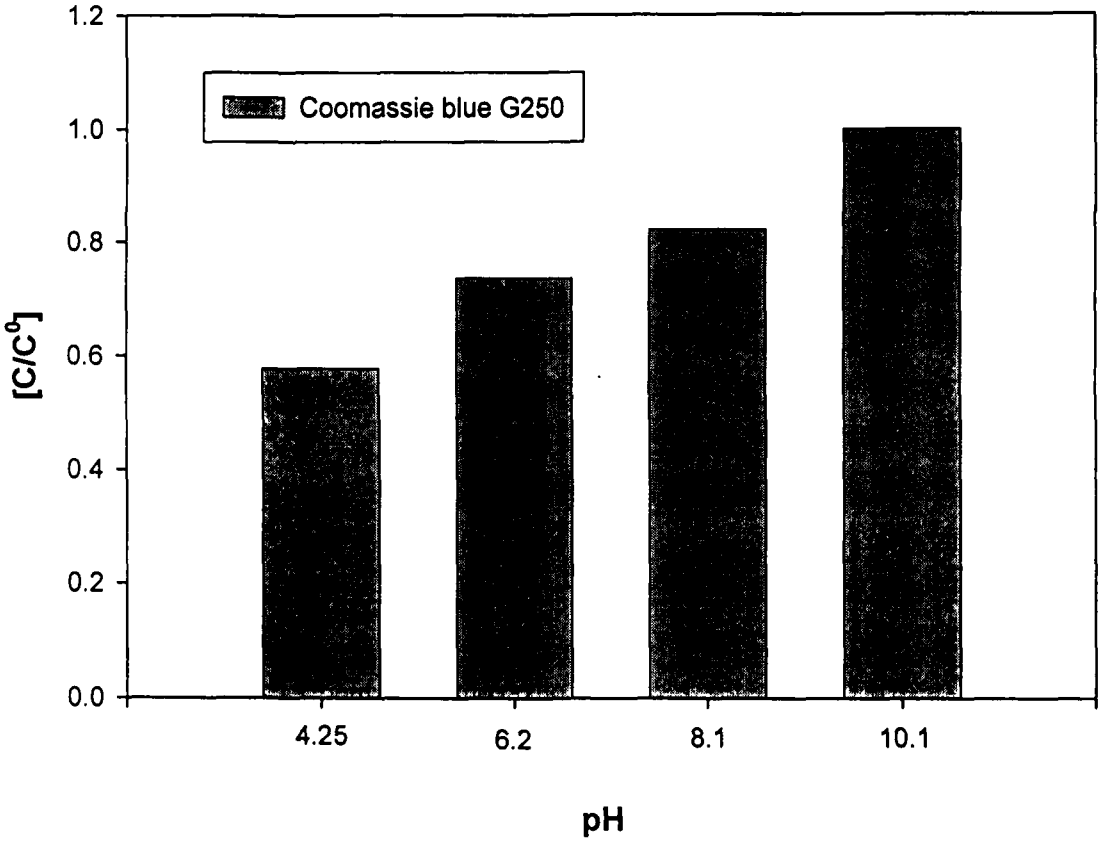


Figure 1.16. Change in concentration as a function of pH on stirring aqueous solution of coommassie blue G250 (1) with photocatalyst in dark for 24 h.

Experimental conditions: 0.5mM coommassie blue G250, V=20 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (4.25, 6.2, 8.1 and 10.1).

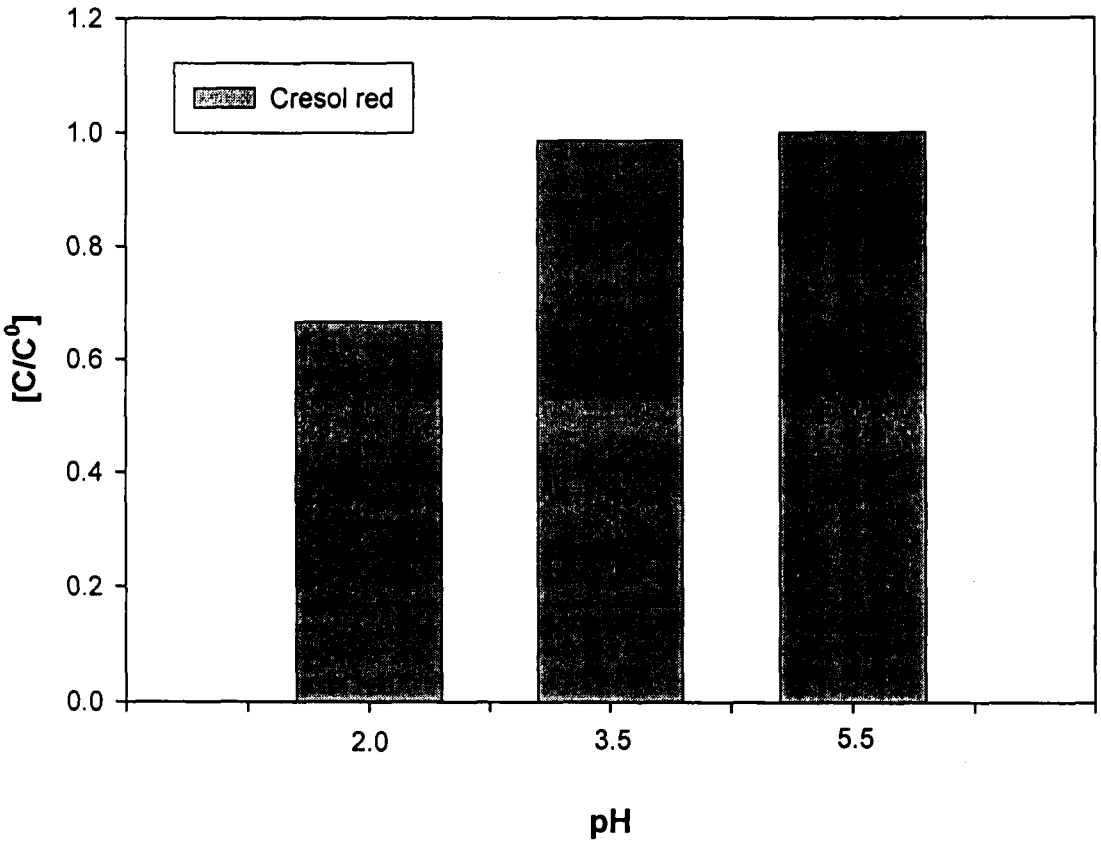


Figure 1.17. Change in concentration as a function of pH on stirring aqueous solution of cresol red (**2**) with photocatalyst in dark for 24 h.

Experimental conditions: 0.3mM cresol red, V=20 mL, photocatalyst: TiO_2 (Hombikat UV100, 1 gL^{-1}), reaction pH (2.0, 3.5 and 5.5).

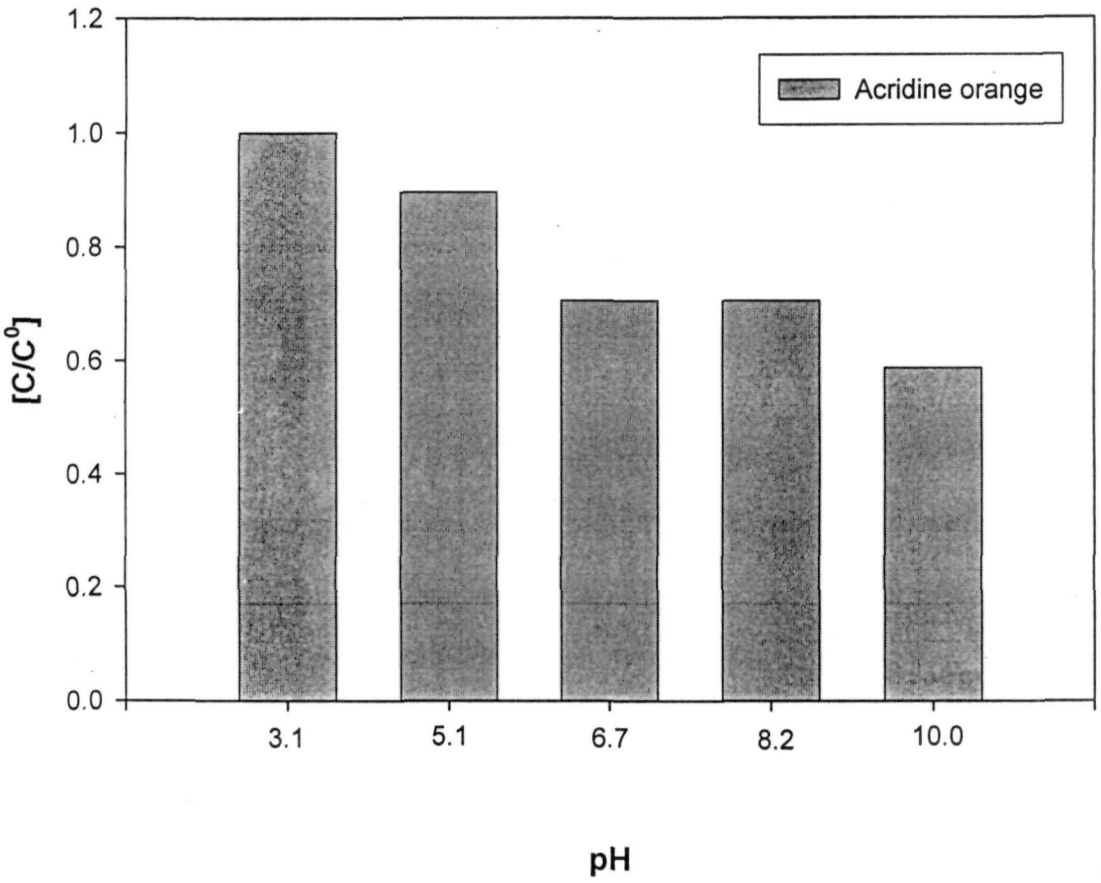


Figure 1.18. Change in concentration as a function of pH on stirring aqueous solution of acridine orange (**3**) with photocatalyst in dark for 24 h.

Experimental conditions: 0.3mM acridine orange, V=20 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (3.1, 5.1, 6.7, 8.2 and 10.0).

$$TiOH + H^+ \longrightarrow TiOH_2^+ \quad [7]$$

$$TiOH + OH^- \longrightarrow TiO^- + H_2O \quad [8]$$

Our results on the photocatalytic degradation and adsorption of the compound indicate that the rates were found to be higher at pH values where maximum adsorption takes place in the dark e.g. compounds **2** (Figs. **1.13, 1.17)** and **3** (Figs. **1.14, 1.18**) except in the case of **1** where slight lower rates were found at pH 4.2 where some loss of the compound was seen due to adsorption (Figs.**1.12, 1.16**).

We have found that some compounds degrade faster at lower pH values (like compounds **2** and **4**) whereas others (like compound **1** and **3**) degrade faster at higher pH values.

All the compounds under investigation contain either amino group or carbonyl group which can be protonated and deprotonated depending on the pH of the reaction mixture.

The higher degradation rate under acidic condition may be due to the fact that the structure orientation of the compound at these pH values are favorable for the attack of the reactive species.

The highest efficiency of degradation in alkaline pH could be attributed to more efficient generation of hydroxyl radical by TiO_2 with increasing concentration of hydroxide ion.

1.4.5 Effect of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of substrate concentration on the

photocatalytic reaction rate. Effect of substrate concentration on the degradation of the dye derivatives, **1 - 4** was studied at different initial concentrations. The degradation rate for the decomposition of compounds, **1 - 4** as a function of substrate concentration employing Degussa P25 (in case of **1**, **3** and **4**) and UV100 (in case of **2**) as photocatalyst is shown in Figs. **1.19 - 1.22**, respectively. It is interesting to note that the rate for the decomposition of dye derivative, **1** increases with the increase in substrate concentration from 0.25 to 0.5 mM and a further increase in substrate concentration from 0.5 to 0.6 mM lead to decrease in the degradation rate. A similar trend for the degradation of dye derivative, **3** as a function of substrate concentration varying from 0.1 to 0.5 mM was observed. On the otherhand in the case of dye derivatives, **2** and **4** the degradation rate was found to decrease continuously with increase in substrate concentration from 0.2 to 0.4 mM (in the case **2**) and 0.1 to 0.4 mM (in the case of **4**).

The decrease in the degradation rate at high concentration may be due to the fact that as the initial concentration of the dye increases, the color of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. The generation of relative amounts of $OH^{\bullet}$ and $O_2^{\bullet -}$ on the surface of the catalyst do not increase as the intensity of light, illumination time and concentration of the catalyst are constant. Conversely, their

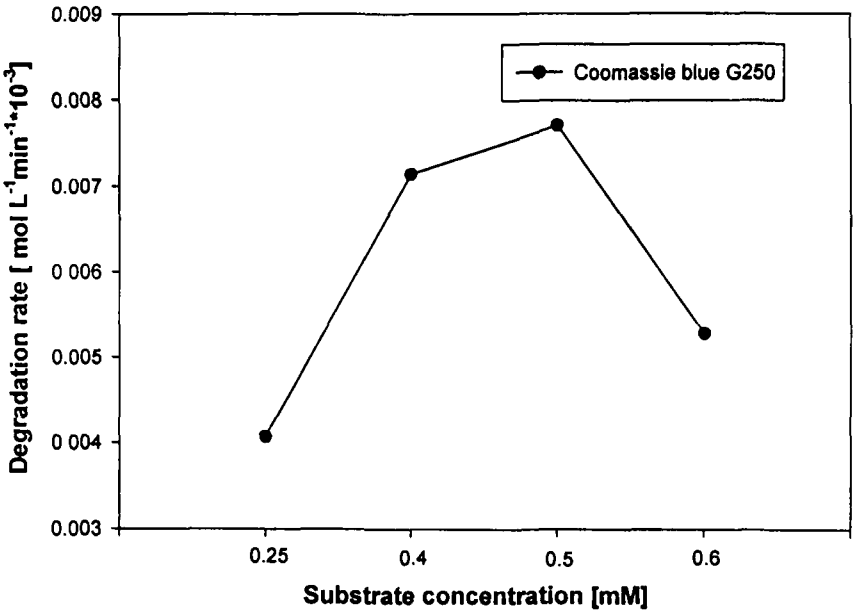


Figure 1.19. Influence of substrate concentration on the degradation rate for the decomposition of coomassie blue G250 (1).

Experimental conditions: substrate concentrations (0.25, 0.4, 0.5 and 0.6 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 75 min.

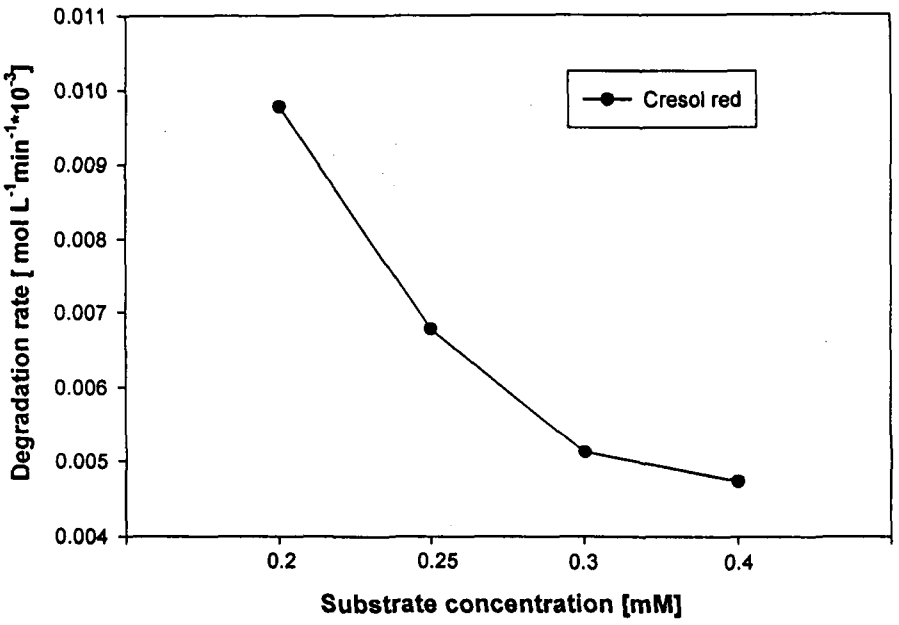


Figure 1.20. Influence of substrate concentration on the degradation rate for the decomposition of cresol red (**2**). Experimental conditions: substrate concentrations (0.2, 0.25, 0.3 and 0.4 mM), V=250 mL, photocatalyst: TiO_2 (Hombikat UV100, 1 gL^{-1}), irradiation time = 65 min.

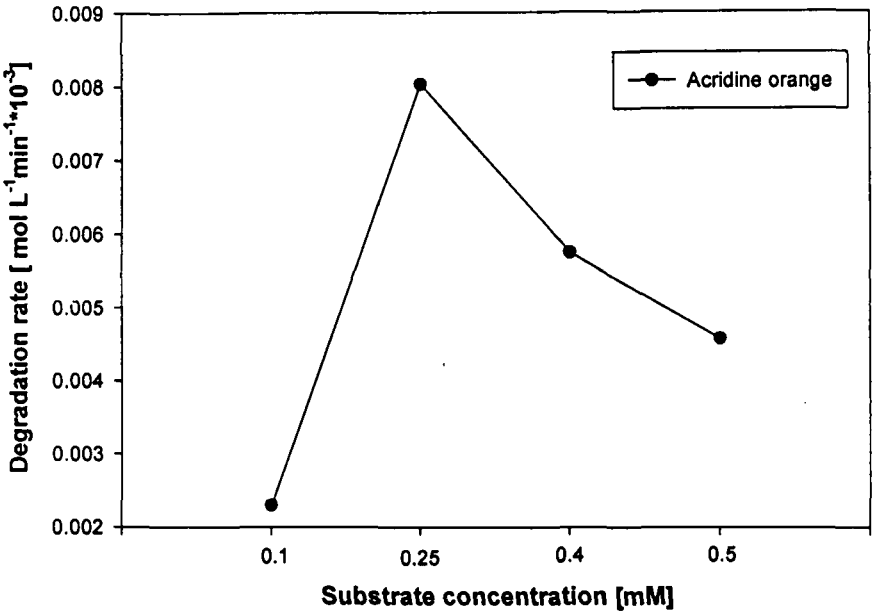


Figure 1.21. Influence of substrate concentration on the degradation rate for decomposition of acridine orange (3).

Experimental conditions: substrate concentrations (0.1, 0.25, 0.4, and 0.5 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 75 min.

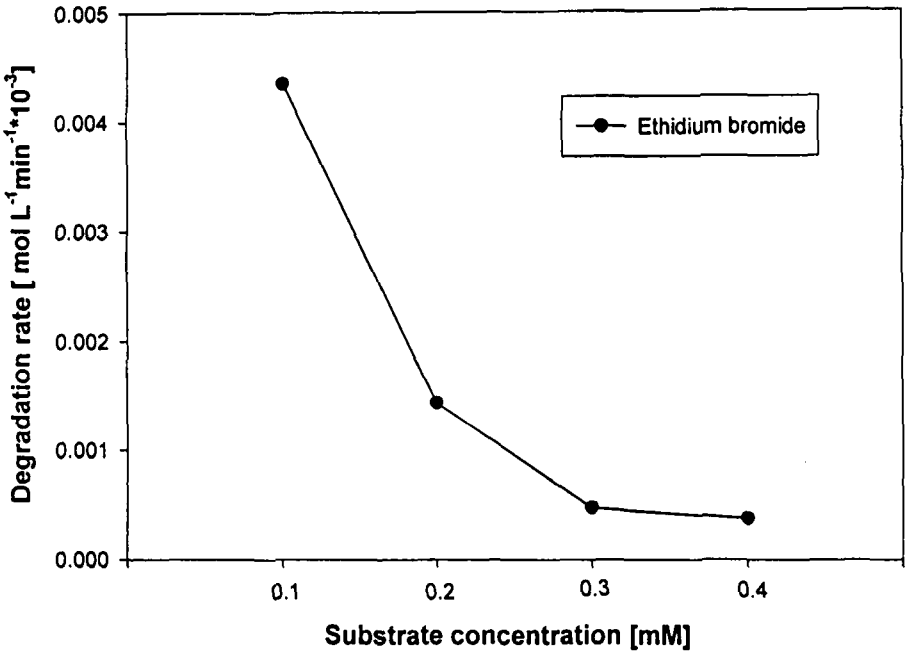


Figure 1.22. Influence of substrate concentration on the degradation rate for decomposition of ethidium bromide (4).

Experimental conditions: substrate concentrations (0.1, 0.2, 0.3, and 0.4 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 195 min.

concentrations will decrease with increase in concentration of the dye as the light photons are largely absorbed and prevented from reaching the catalyst surface by the dye molecules. Consequently, for a given mass of TiO_2, the degradation efficiency of the dye decreases as the dye concentration increases.

1.4.7. Effect of electron acceptors

One practical problem in using TiO_2 as a photocatalyst is the undesired electron / hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and represent the major energy - wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron - hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effects such as i.e. 1) to increase the number of trapped electrons and consequently avoid recombination 2) to generate more radicals and other oxidizing species 3) to increase the oxidation rate of intermediate compounds and 4) to avoid problems caused by low oxygen concentration. In highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of electron acceptors to enhance the degradation rate may often be justified. With this view, we have studied the effect of electron acceptors such as ammonium persulphate, potassium bromate and hydrogen peroxide in presence of TiO_2 in order to look the effect of these additives on the degradation of dyes under investigation. Figs.

1.23 - 1.26 show the degradation rate for the decomposition of dyes, **1 - 4** in the presence of different electron acceptors in addition to TiO_2 and atmospheric oxygen.

For compounds, **1** and **3**, the effect of two electron acceptors such as H_2O_2 and $KBrO_3$ were investigated. In the case of **1**, only H_2O_2 and in the case of **3**, both additives (H_2O_2 and $KBrO_3$) enhanced the degradation rate markedly as shown in Fig. **1.23** and **1.25** respectively. Whereas, for compounds, **2** and **4**, the effect of three electron acceptors such as H_2O_2, $KBrO_3$ and $(NH_4)_2S_2O_8$ were investigated. In the case of **2**, only $KBrO_3$ and in the case of **4**, all three additives enhanced the degradation rate as shown in Fig. **1.24** and **1.26**. The dye derivatives, **1** and **3** in the presence of ammonium persulphate found to coagulate with TiO_2 powder leading to decrease in absorption intensity of dye therefore the effect of this additive on degradation of these dye derivatives could not be studied.

The electron acceptors used are known to generate hydroxyl radicals and reactive species by the mechanisms shown in eqs 9-13;

$$H_2O_2 + e^-_{CB} \rightarrow {}^{\bullet}OH + OH^- \quad [9]$$

$$BrO_3 + 2H^+ + e^-_{CB} \rightarrow BrO^{-\bullet}_2 + H_2O \quad [10]$$

$$BrO_3 + 6H^+ + 6\, e^-_{CB} \rightarrow [BrO^-_2, HOBr] \rightarrow Br + 3H_2O \quad [11]$$

$$S_2O_8^{2-} + e^-_{cb} \rightarrow SO_4^{2-} + SO^{\bullet-}_4 \quad [12]$$

$$SO^{\bullet-}_4 + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \quad [13]$$

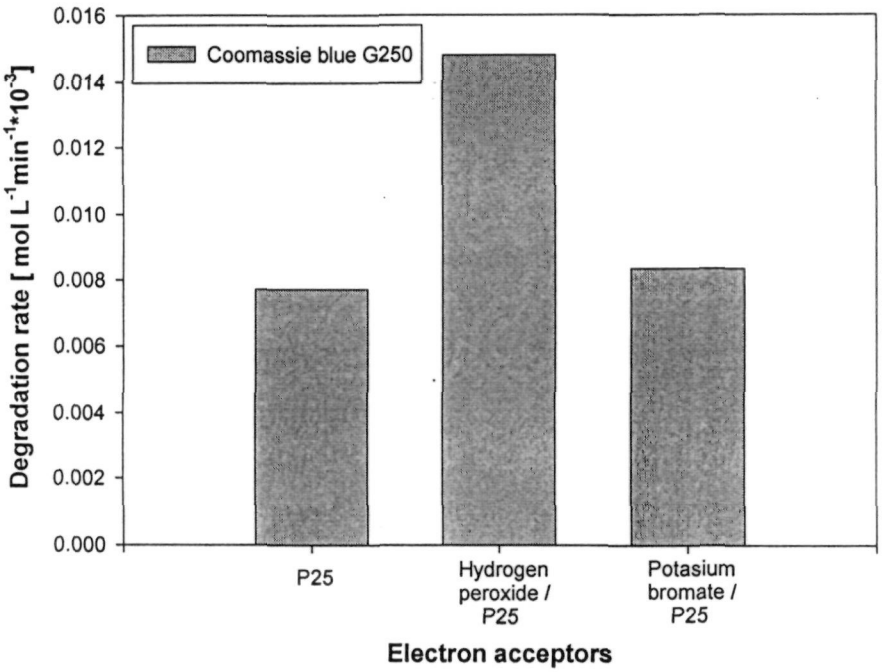


Figure 1.23. Comparison of degradation rate for the decomposition of coomassie blue G250 (**1**) in the presence of different electron acceptors.

Experimental conditions: 0.5 mM coomassie blue G250, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), H_2O_2 (10 mM), irradiation time = 75 min.

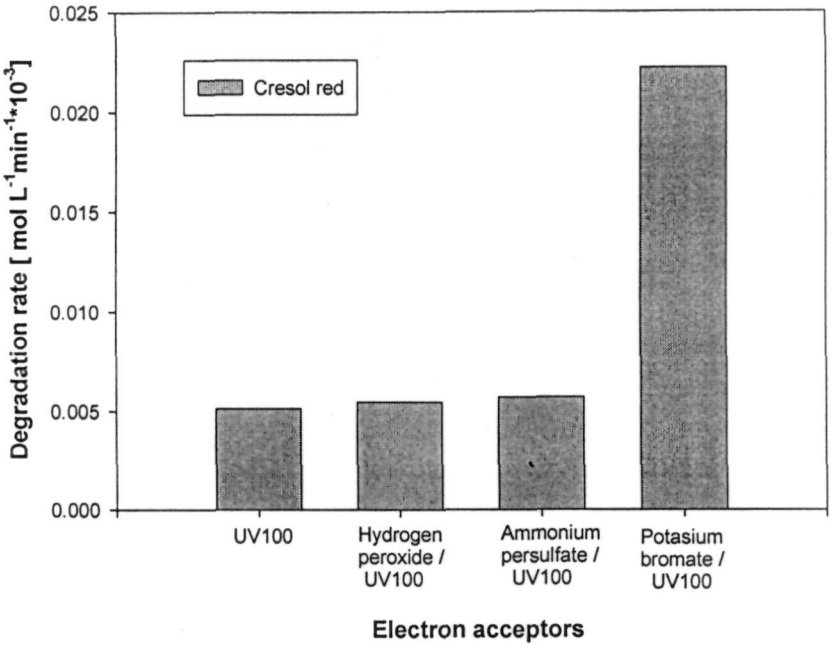


Figure 1.24. Comparison of degradation rate for the decomposition of cresol red (**2**) in the presence of different electron acceptors.

Experimental conditions: 0.3 mM cresol red, V=250mL, photocatalyst: TiO_2 (Hombikat UV100, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 65 min.

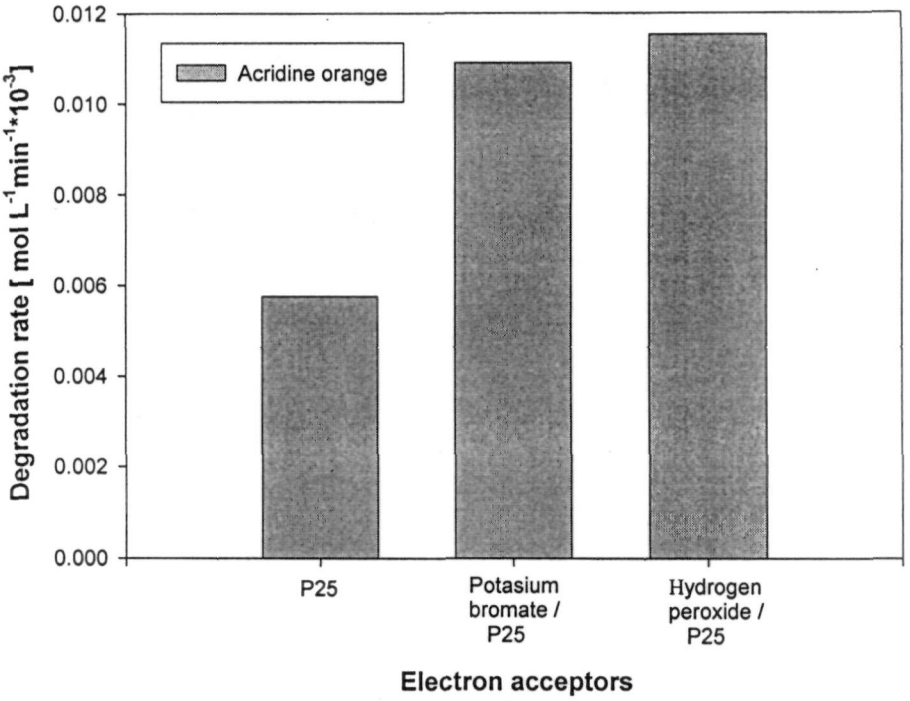


Figure 1.25. Comparison of degradation rate for the decomposition of acridine orange (**3**) in the presence of different electron acceptors.

Experimental conditions: 0.4 mM acridine orange, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), H_2O_2 (10 mM), irradiation time = 75 min.

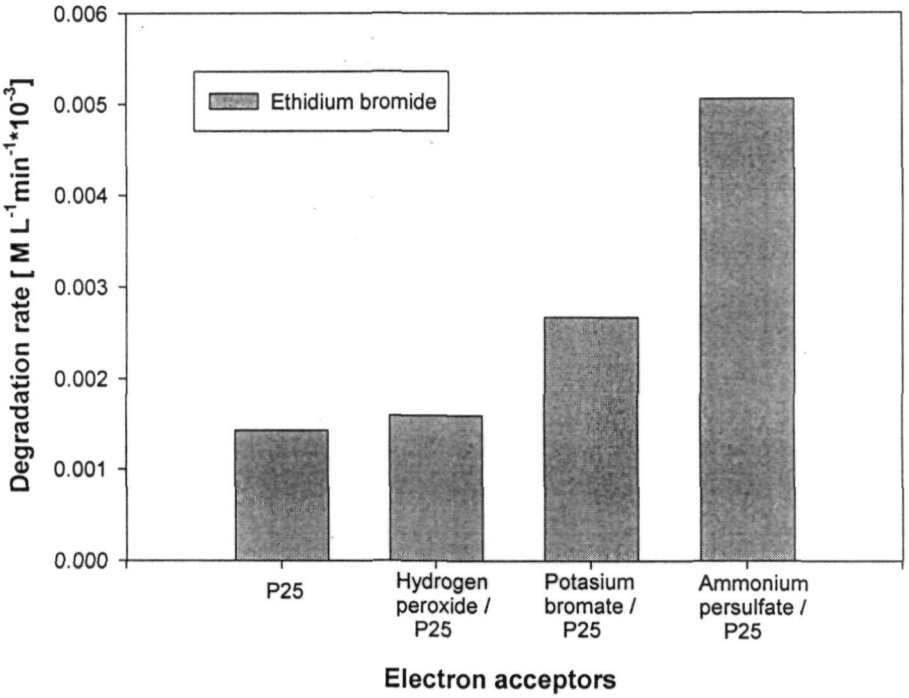


Figure 1.26. Comparison of degradation rate for the decomposition of ethidium bromide (**4**) in the presence of different electron acceptors.

Experimental conditions: 0.2 mM ethidium bromide, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 195 min.

The respective one-electron reduction potentials of different species are: E ($O_2/O_2^{\bullet-}$) = -155mV, E ($H_2O_2/HO^{\bullet}$) = 800mV, E (BrO_3^- /$BrO^{\bullet-}_2$) = 1150 mV, and E ($S_2O_8^{2-}$ /$SO_4^{\bullet-}$) = 1100 mV.[62] From the thermodynamic point of view all employed additives should therefore be more efficient electron acceptors than molecular oxygen.

The effective electron acceptor ability of $KBrO_3$ has been *observed in number of studies reported before.*[57,58,63] *The reason can* be attributed to the number of electrons it reacts as shown in eq. 10-11. The reduction of bromate ions by electrons does not lead directly to the formation of hydroxyl radicals, but rather to the formation of other reactive radicals or oxidizing agents eg. BrO^-_2 and HOBr. Furthermore, bromate ions by themselves can act as oxidizing agents. Lindner has proposed a mechanism for the photocatalytic degradation of 4-chlorophenol in the presence of bromate ions considering direct oxidation of the substrate by bromate ions.[64] A similar mechanism might also be operative in the model compounds used in these studies.

1.4.7 Photocatalysis of TiO_2 suspension containing dye derivatives under sunlight

For practical applications of wastewater treatment based on these processes, the utilization of sunlight is preferred. Hence the aqueous suspension of TiO_2 containing dye was exposed to solar radiation. Fig. **1.27 - 1.30** show the comparison of change in

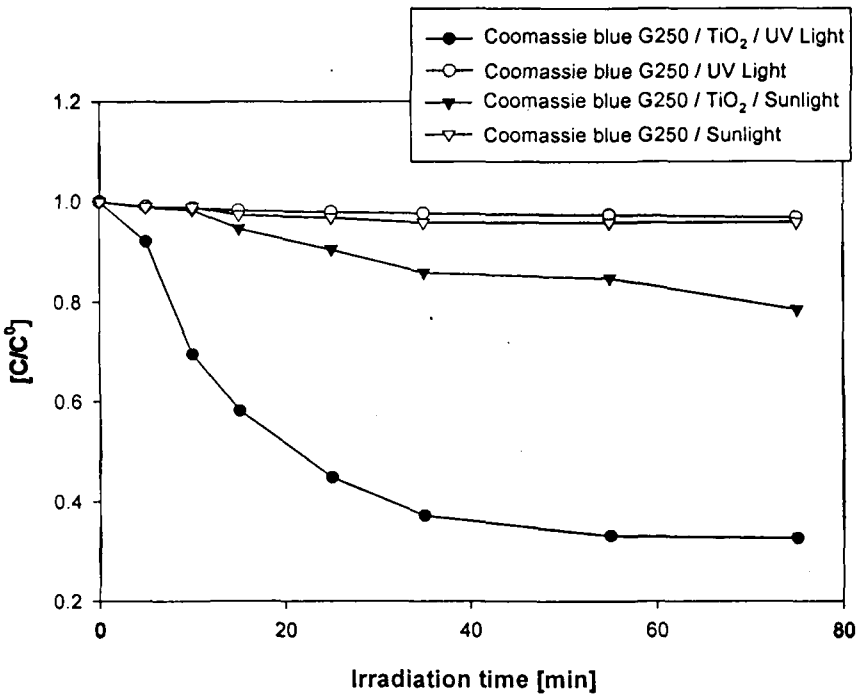


Figure 1.27. Comparision of change in concentration as a function of time for irradiation of an aqueous suspension of coomassie blue G250 (**1**) in the presence and absence of photocatalyst under sunlight and UV light source.

Experimental conditions: a) UV Light: 0.5 mM coomassie blue G250, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, continuous atmospheric oxygen purging and stirring, irradiation time = 75 min.

b) Sunlight: 0.5 mM coomassie blue G250, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, continuous atmospheric oxygen purging and stirring, illumination time = 75 min.

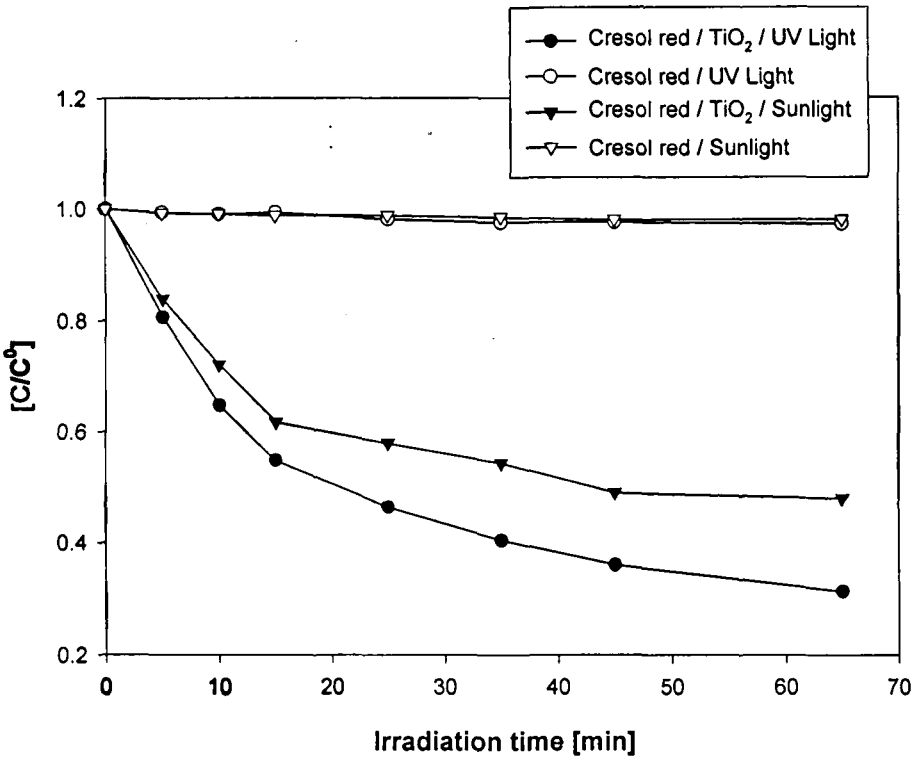


Figure 1.28. Comparision of change in concentration as a function of time for irradiation of an aqueous suspension of cresol red (**2**) in the presence and absence of photocatalyst under sunlight and UV light source.

Experimental conditions: a) UV Light: 0.3 mM cresol red, V=250 mL, photocatalyst: TiO_2 (Hombikat UV100, $1gL^{-1}$), immersion well photoreactor, 125 W medium pressure Hg lamp, continuous atmospheric oxygen purging and stirring, illumination time = 65 min.

b) Sunlight: 0.3 mM cresol red, V=250 mL, photocatalyst: TiO_2 (Hombikat UV100, $1gL^{-1}$), immersion well photoreactor, continuous atmospheric oxygen purging and stirring, irradiation time = 65 min.

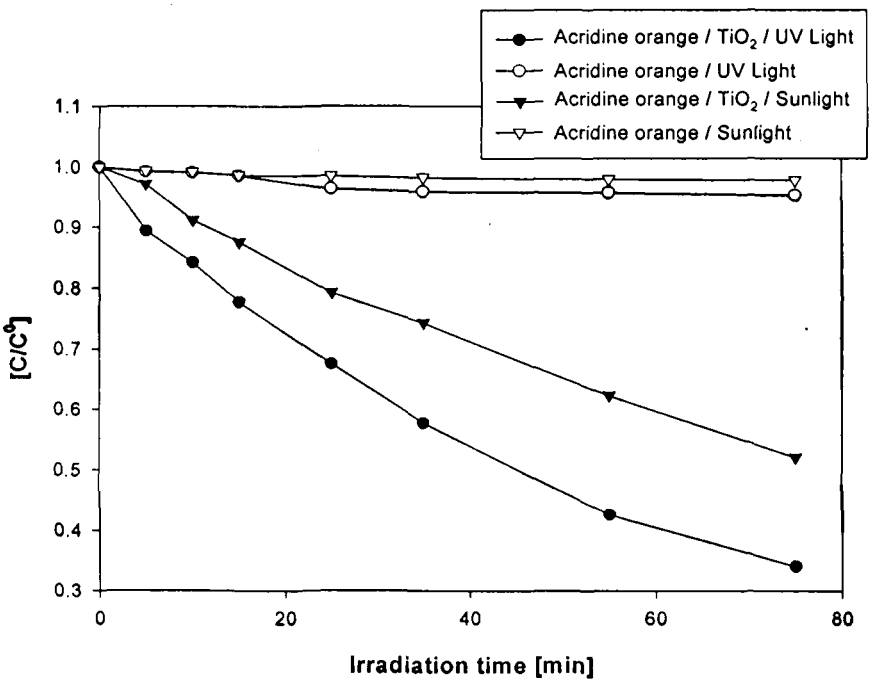


Figure 1.29. Comparision of change in concentration as a function of time for irradiation of an aqueous suspension of acridine orange (**3**) in the presence and absence of photocatalyst under sunlight and UV light source.

Experimental conditions: a) UV Light: 0.4 mM acridine orange, V=250 mL, photocatalyst: TiO_2 (Degussa P25, $1gL^{-1}$), immersion well photoreactor, 125 W medium pressure Hg lamp, continuous atmospheric oxygen purging and stirring, irradiation time = 75 min.

b) Sunlight: 0.4 mM acridine orange, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, continuous atmospheric oxygen purging and stirring, illumination time = 75 min.

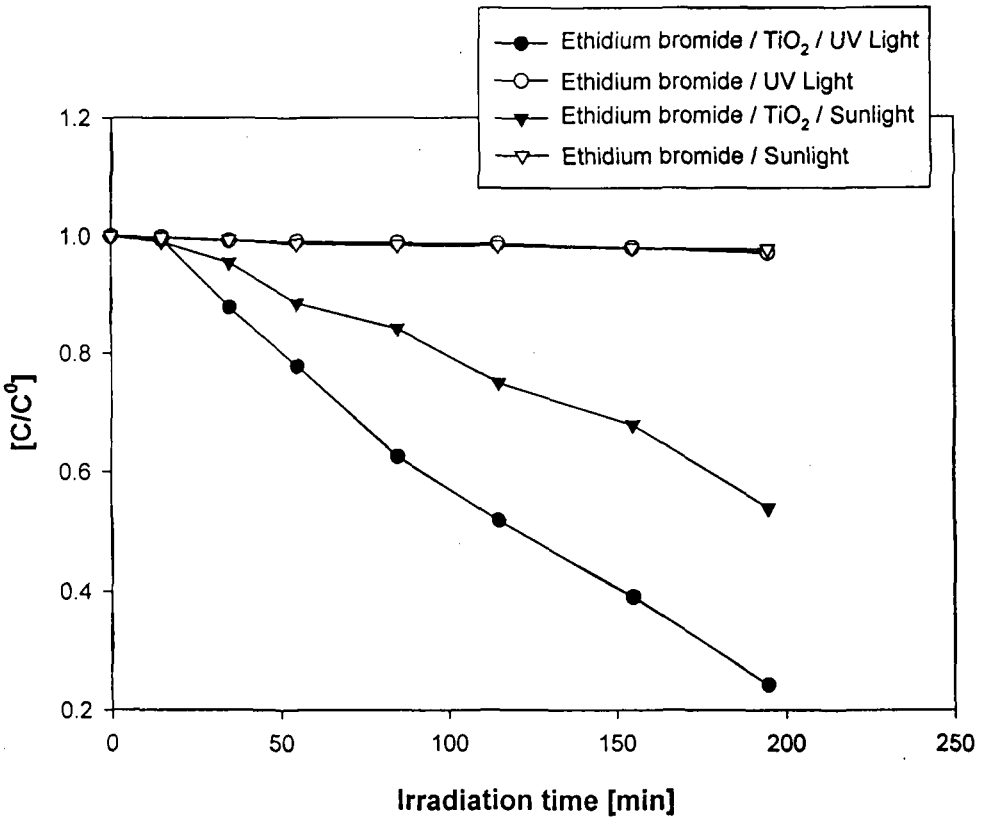


Figure 1.30. Comparison of change in concentration as a function of time for irradiation of an aqueous suspension of ethidium bromide (**4**) in the presence and absence of photocatalyst under sunlight and UV light source.

Experimental conditions: a) UV Light: 0.2 mM ethidium bromide, V=250 mL, photocatalyst: TiO_2 (Degussa P25, $1 gL^{-1}$), immersion well photoreactor, 125 W medium pressure Hg lamp, continuous atmospheric oxygen purging and stirring, irradiation time = 195 min.

b) Sunlight: 0.2 mM ethidium bromide, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, continuous atmospheric oxygen purging and stirring, illumination time = 195 min.

concentration as a function of time on illumination of an aqueous suspension of dye derivatives in the absence and presence of TiO_2 under sunlight and UV light source. All the dyes under investigation efficiently degrade in the presence of UV light source as compared with that of sunlight. Blank experiments were carried in the absence of TiO_2 where no observable loss of the dye was found as shown in Figs. **1.27 – 1.30.**

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Chapter 2

PHOTOCHEMICAL REACTIONS OF FOUR SELECTED PESTICIDE DERIVATIVES, 2-(2,4,5-TRICHLOROPHENOXY) PROPIONIC ACID, DICHLOROPROP-P, 2,4,6-TRICHLOROPHENOL AND 4-CYANOPHENOL IN AQUEOUS SUSPENSIONS OF TITANIUM DIOXIDE[1]

2.1 Abstract

The photochemical reactions of four selected pesticide derivatives such as 2-(2,4,5-trichlorophenoxy)propionic acid (Fenoprop, **1**), dichloroprop-P (**2**), 2,4,6-trichlorophenol (2,4,6-TCP, **3**) and 4-cyanophenol (**4**) has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was investigated by monitoring the change in substrate concentration employing UV-spectroscopic analysis technique as a function of irradiation time. The degradation was studied under different conditions such as different types of TiO_2, reaction pH, catalyst concentration, substrate concentration and in the presence of electron acceptors such as hydrogen peroxide, ammonium persulphate and potassium bromate besides atmospheric oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst, Degussa P25 was found to be more efficient for the degradation of all the pollutants under investigation.

2.2 Introduction

In recent years, rapid industrial growth and use of advanced chemicals such as pesticides, herbicides and other organic pollutants is the cause of accumulation of these organic substances in the ground and surface water, which is a matter of great concern for the scientific and regulation authorities. These pollutants, due to their chemical stability, resistant to biodegradation and with sufficient water solubility penetrate deep into the ground water[2-4]. To combat this critical environmental hazard advanced methods are in demand for effective treatment of polluted ground and surface water. Detoxification technologies have to achieve the complete decomposition of target molecules.

The phenoxy derivatives such as 2-(2,4,5-trichlorophenoxy) propionic acid (Fenoprop, **1**) and dichloroprop-P (**2**) are selective pre and post harvest emergence herbicide. They are used in the control of woody plants on uncropped land[5] and as a plant growth regulator.[6] The phenol derivative like 2,4,6- Trichlorophenol (**3**) is also used as fungicide, bactericide and preserative.[7,8] It is freely soluble in water and is reasonably anticipated to be a human carcinogen.[9]

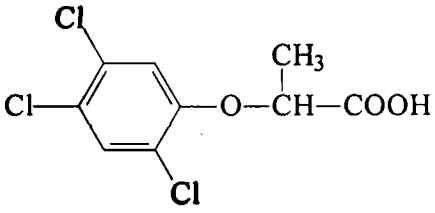
Photocatalysed degradation of phenoxyacetic acid and their chloroderivatives has been extensively studied.[10-19] For example,

photoredox reaction and photocatalysed degradation of phenoxyacetic acid over supported TiO_2 in a flow system has been reported.[10,11] Herrmann and coworkers[15] have reported a TiO_2 based solar photocatalytic detoxification of 2,4-D and Pichat et al.[18] proposed a degradation pathway. Photodegradation of 2,4,6 trichlorophenol has also been reported earlier.[20,21] To best of our knowledge no efforts have been made to look into the degradation of chloroderivatives of phenoxy propionic acid. With this view we have taken a detailed study on the photodegradation of two selected propionic acid derivatives like 2-(2,4,5-trichlorophenoxy)propionic acid (Fenoprop, **1**) and dichloroprop-P (**2**) and two phenol derivatives such as 2,4,6 trichlorophenol (**3**) and 4-cyanophenol (**4**) (chart **2.1**) in aqueous suspensions of TiO_2 under a variety of conditions.

2.3 Experimental

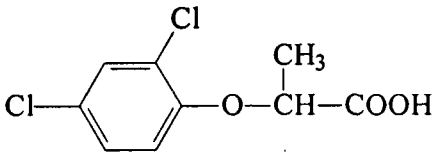
2.3.1 Reagent and chemicals

All the pesticide derivatives, **1 - 4** were purchased from Sigma-Aldrich, and used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst titanium dioxide, Degussa P25 (Degussa AG)[22] was used in most of the experiments, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH)[23] and PC500 (Millennium inorganic chemicals)[23] were used for comparative studies. The other



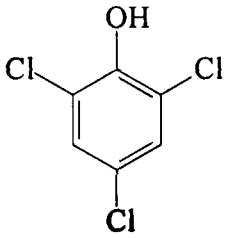
2-(2,4,5-trichlorophenoxy)propionic acid

(1)



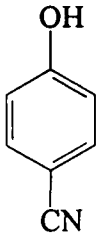
Dichloroprop-P

(2)



2,4,6-trichlorophenol

(3)



4-cyanophenol

(4)

Chart : 2.1. Chemical Structure and Chemical name

chemicals used in this study such as NaOH, HNO_3, $KBrO_3$, H_2O_2 and $(NH_4)_2S_2O_8$ were obtained from Merck.

2.3.2 Procedure

Solution of pesticide derivatives, **1 - 4** of desired concentrations were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass was used. For irradiation experiment, 250 mL solution of the compound of desired concentration was filled into the reactor and required amount of TiO_2 was added. The solution was stirred for at least 10 minutes in the dark to allow equilibration of the system, so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with atmospheric oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (radiant flux≈2590 μWcm^{-2}). IR and short wavelength UV radiations were eliminated by water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation for analysis after centrifugation.

2.3.3 Analysis

The degradation of the model compounds, **1 - 4** was followed by measuring the absorption intensity at their λ_{max} as a function of irradiation time using Shimadzu UV-Vis Spectrophotometer (Model 1601).

2.4 Results and Discussion

2.4.1 Photocatalysis of aqueous suspensions of pesticide derivatives, 1 - 4 containing TiO_2

Irradiation of an aqueous suspension of the pesticide derivatives, **1 – 4** in the presence of TiO_2 (Degussa P25, $1gL^{-1}$) with a 125 W medium pressure mercury lamp under continuous bubbling of atmospheric oxygen lead to decrease in absorption intensity as a function time. This adsorption intensity is used to calculate the concentration using the standard calibration curve, which in turn is used to calculate the rate constants. Figs. **2.1 - 2.4** show the change in concentration as a function of time for irradiation of aqueous suspensions of compounds, **1 – 4** in the presence and absence of photocatalyst. It could be seen from the figures that all the compounds undergo degradation (55 - 86%) after 60 minutes of irradiation, whereas, no observable loss of the compound takes place when irradiated in the absence of photocatalyst.

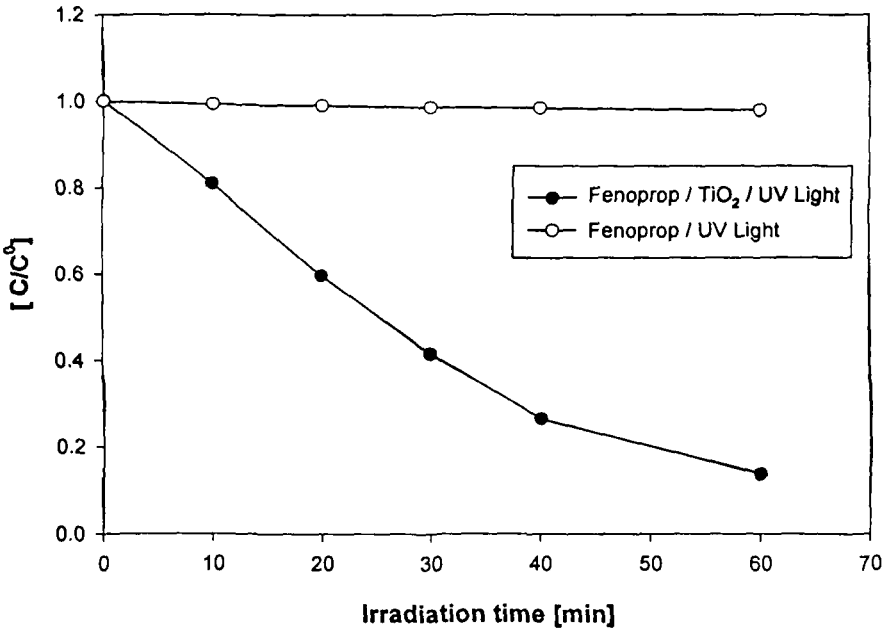


Figure 2.1. Change in concentration as a function of time for irradiation of an aqueous suspension of fenoprop (1) in the presence and absence of photocatalyst.

Experimental conditions: 0.5 mM fenoprop, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 289.5 nm, continuous atmospheric oxygen purging and stirring, irradiation

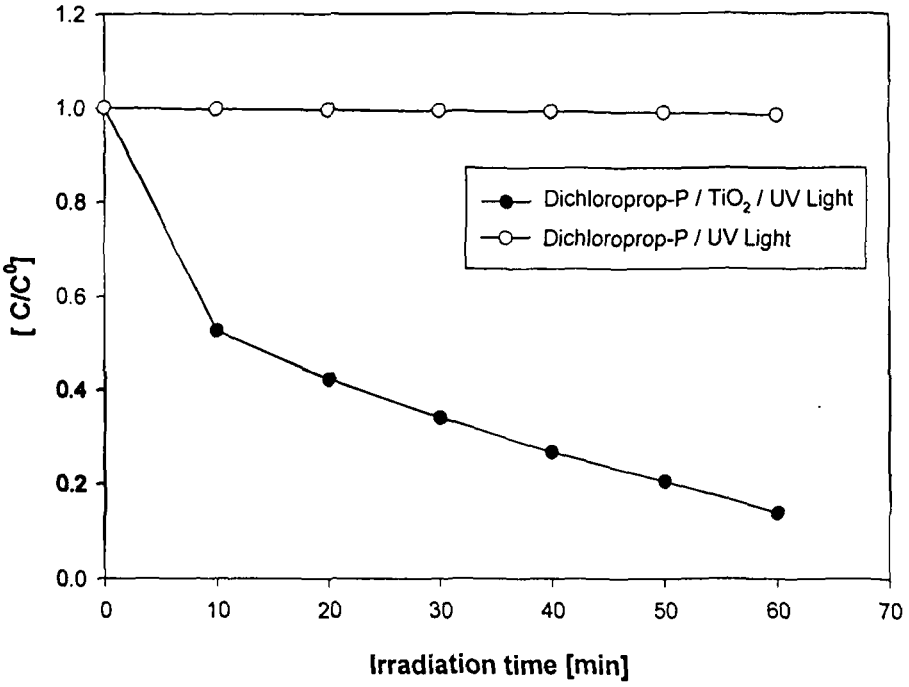


Figure 2.2. *Change in concentration as a function of* time for irradiation of an aqueous suspension of dichloroprop-P (**2**) in the presence and absence of photocatalyst.

Experimental conditions: 0.4 mM dichloroprop-P, V=250 mL, photocatalyst: TiO_2 (Degussa P25, $1gL^{-1}$), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 284 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 60 min.

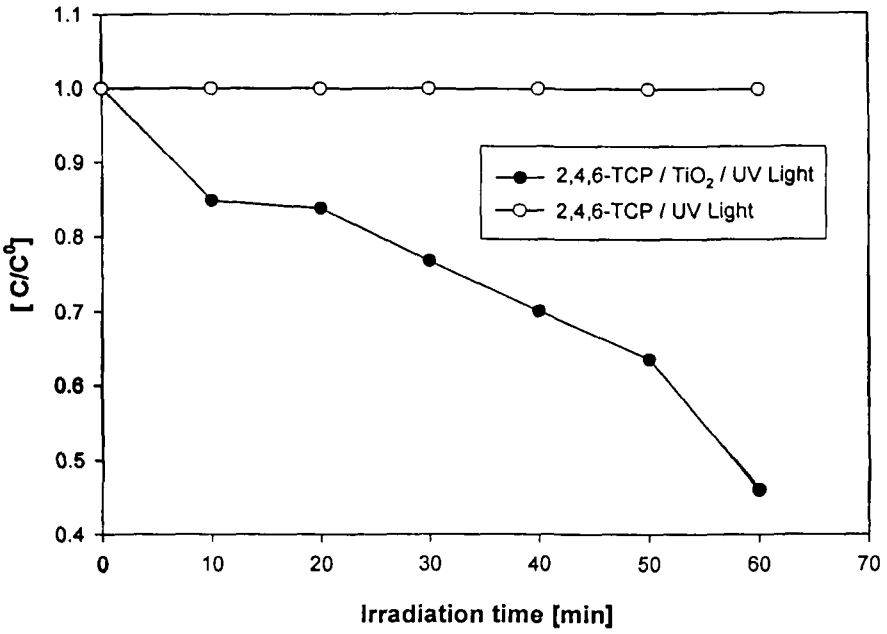


Figure 2.3. Change in concentration as a function of time for irradiation of an aqueous suspension of 2,4,6-TCP (3) in the presence and absence of photocatalyst.

Experimental conditions: 0.8 mM 2,4,6-TCP, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 294 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 60 min.

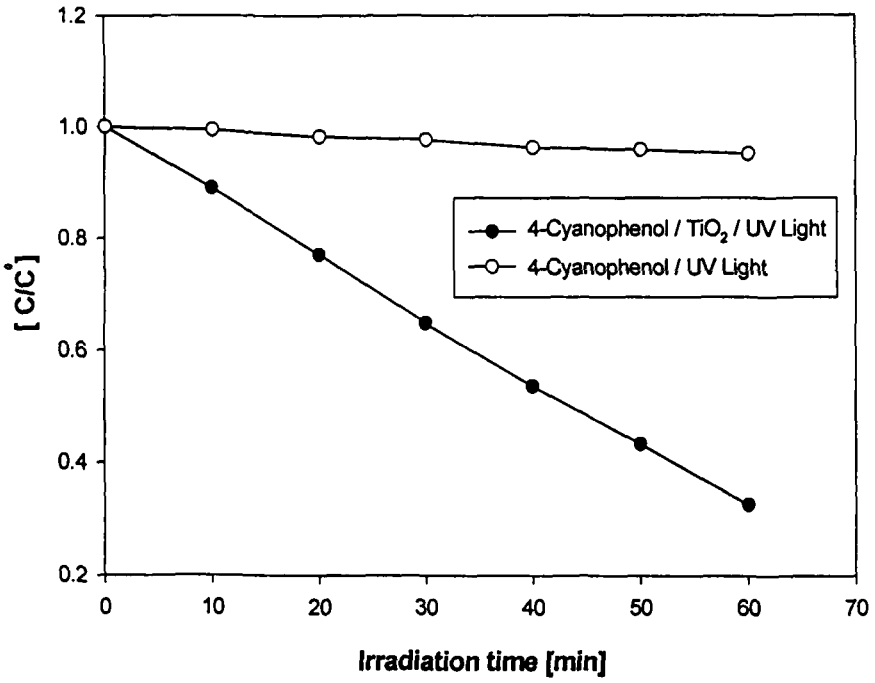


Figure 2.4. Change in concentration as a function of time for irradiation of an aqueous suspension of 4-cyanophenol (**4**) in the presence and absence of photocatalyst.

Experimental conditions: 0.5 mM 4-cyanophenol, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 247 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 60 min.

The degradation curves for compounds, **1 - 3** (Figs. **2.1 - 2.3**) can be fitted reasonably well by an exponential decay curve suggesting the first order kinetics, whereas, the degradation curve for compound **4** (Fig. **2.4**) can be fitted reasonably well by an exponential decay curve suggesting zero order kinetics. For the sake of uniformity we have considered this curve also as a first order kinetics. For each experiment, the degradation rate constant for compounds, **1 – 4** was calculated from the plot of the natural logarithm of the concentration of the model compound as a function of irradiation time. This rate constant was used to calculate the degradation rate for decomposition of the pollutants using formula given below,

$$-d[C]/dt = kc^n \qquad [1]$$

C = concentration, k = rate constant, c = concentration of the pollutant, n = order of reaction.

The degradation rate for the first order reaction was calculated in terms of mole L^{-1} min^{-1}.

Controlled experiments were carried out in all cases by irradiating aqueous solution of the pollutants in the absence of photocatalyst, where no observable loss of the compound takes place. The zero irradiation time reading was obtained from blank solutions

kept in the dark, but otherwise treated similarly to the irradiated solutions.

2.4.2 Comparison of different photocatalysts

The photocatalytic activity of three different commercially available TiO_2 (namely Degussa P25, Hombikat UV100 and Millennium Inorganic PC500) was tested for the degradation of all the pesticides under investigation. Fig. **2.5 – 2.8** show the degradation rate for the decomposition of pollutants, **1 - 4** in the presence of different photocatalysts. It has been observed that the degradation of all pollutants proceed much more rapidly in the presence of Degussa P25 as compared with other TiO_2 samples.

The reason for better photocatalytic activity of mixed phase titania photocatalyst, Degussa P25 could be attributed on the basis that 1) the smaller band gap of rutile extends the usual range of photoactivity into the visible region 2) the stabilization of charge separation by electron transfer from rutile to anatase slows the recombination 3) the small size of the rutile crystallites facilitates the electron transfer.[24]

In all following experiments, Degussa P25 was used as photocatalyst since this material exhibited the highest over all activity for the degradation of the pesticide under investigation in this chapter.

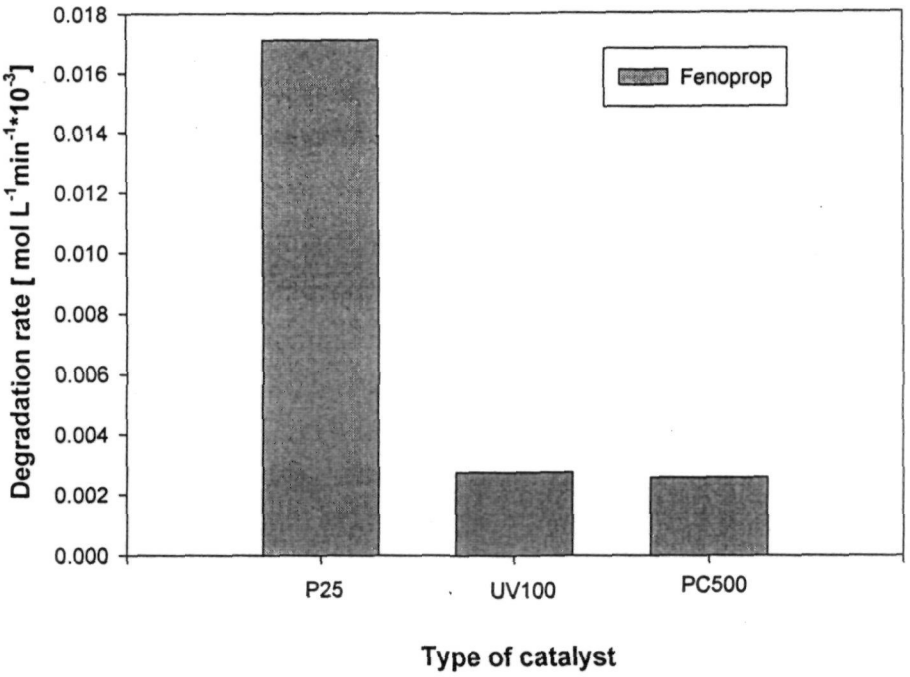


Figure 2.5. Comparison of degradation rate of the decomposition of fenoprop (**1**), in the presence of different types of catalysts.

Experimental conditions: 0.5 mM fenoprop, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC500 (1 gL^{-1}), light source 125 W medium pressure Hg lamp, immersion well photoreactor, continuous atmospheric oxygen purging and stirring, irradiation time = 60 min.

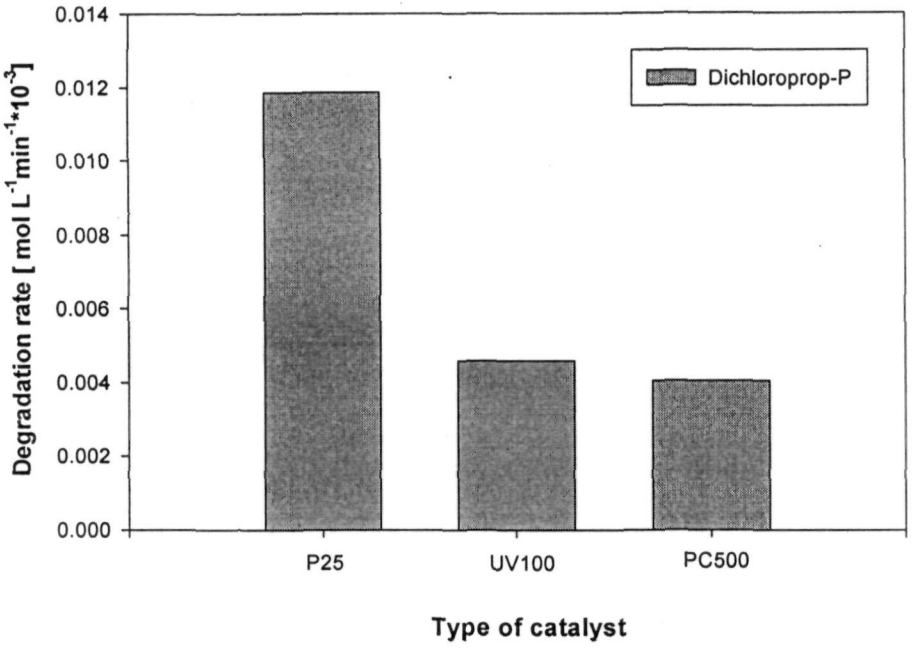


Figure 2.6. Comparison of degradation rate of the decomposition of dichloroprop-P (**2**), in the presence of different types of catalysts.

Experimental conditions: 0.4 mM dichloroprop-P , V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC500 (1 gL^{-1}), light source 125 W medium pressure Hg lamp, immersion well photoreactor, continuous atmospheric oxygen purging and stirring, irradiation time = 60 min.

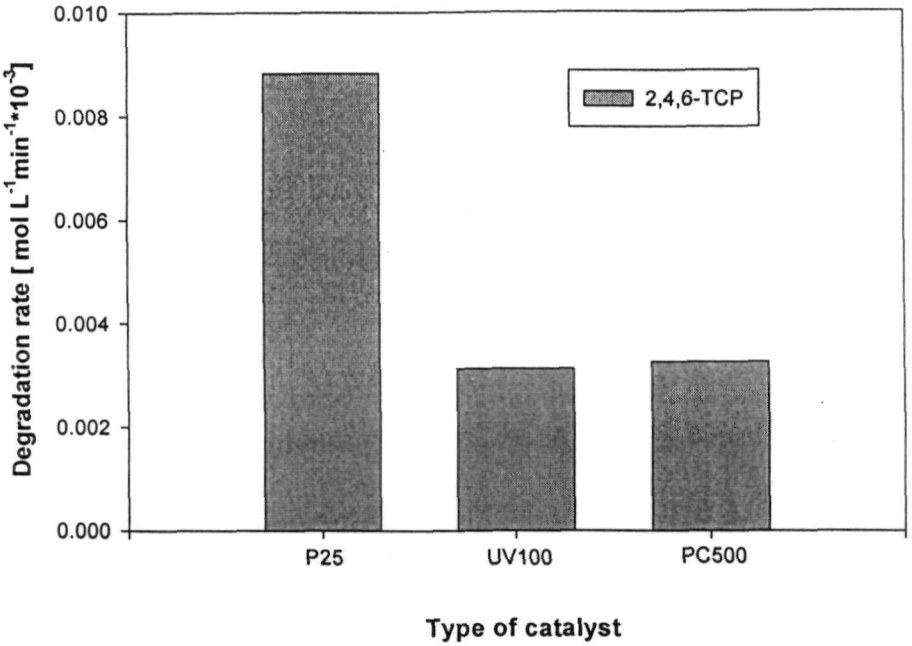


Figure 2.7. Comparison of degradation rate of the decomposition of 2,4,6-TCP (**3**), in the presence of different types of catalysts.

Experimental conditions: 0.8 mM 2,4,6-TCP , V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC500 (1 gL^{-1}), light source 125 W medium pressure Hg lamp, immersion well photoreactor, continuous atmospheric oxygen purging and stirring, irradiation time = 60 min.

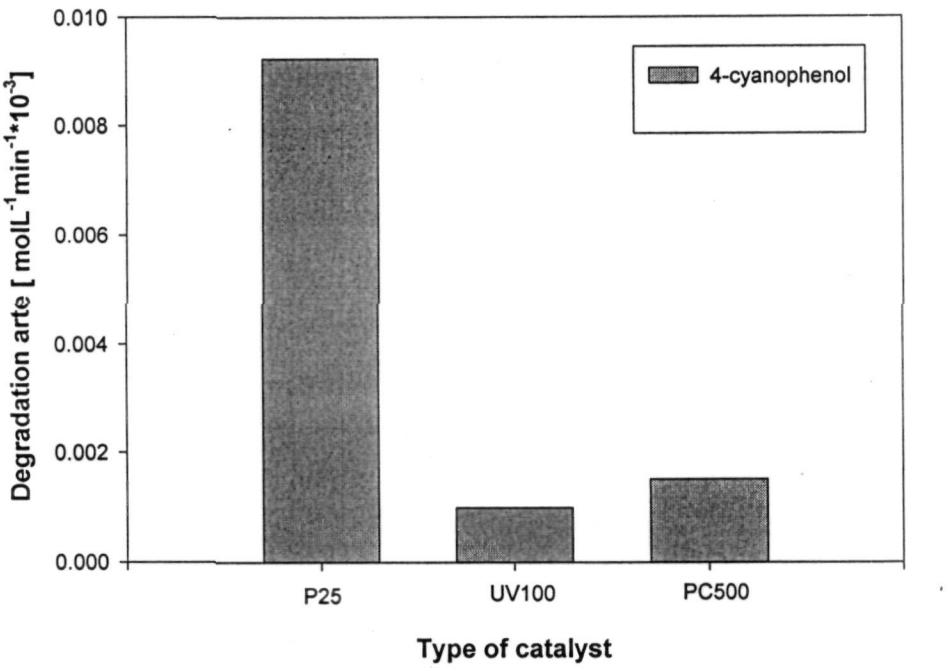


Figure 2.8. Comparison of degradation rate of the decomposition of 4-cyanophenol (**4**), in the presence of different type of catalysts.

Experimental conditions: 0.5 mM 4-cyanophenol, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC500 (1 gL^{-1}), light source: 125 W medium pressure Hg lamp, immersion well photoreactor, continuous air purging and stirring, irradiation time = 60 min.

2.4.3 pH Effect

The photocatalytic degradation of the model compounds such as Fenoprop (**1**), dichloroprop-P (**2**), 2,4,6-TCP (**3**) and 4-cyanophenol (**4**) was investigated at different pH values, which is one of the most important parameter in heterogeneous photocatalysis, since it influences the surface charge properties of the photocatalyst and therefore the adsorption behavior of the pollutants.[25,26]

Employing Degussa P25 as photocatalyst the decomposition of the compounds, **1 - 4** in the aqueous suspension of TiO_2 was studied at different pH values. Figs. **2.9 – 2.12** show the degradation rate for the decomposition of the pesticide derivatives, **1 – 4** as a function of reaction pH. The degradation rate for the decomposition of the pesticide derivatives, **1 - 3** as a function of reaction pH was found increase with the increase in pH and highest efficiency was observed at pH 10.2, 9.6 and 9.7 for compounds, **1**, **2** and **3** respectively in the pH range studied. However, in case of pesticide derivative, **4** the degradation rate was found to decreases with the increase in reaction pH and highest efficiency was found at reaction pH 3.

The adsorption of compounds, **1 – 4** on the surface of the photocatalyst at different pH values between 2 to 10 was investigated by stirring aqueous suspensions of the compounds in the dark for 24 h

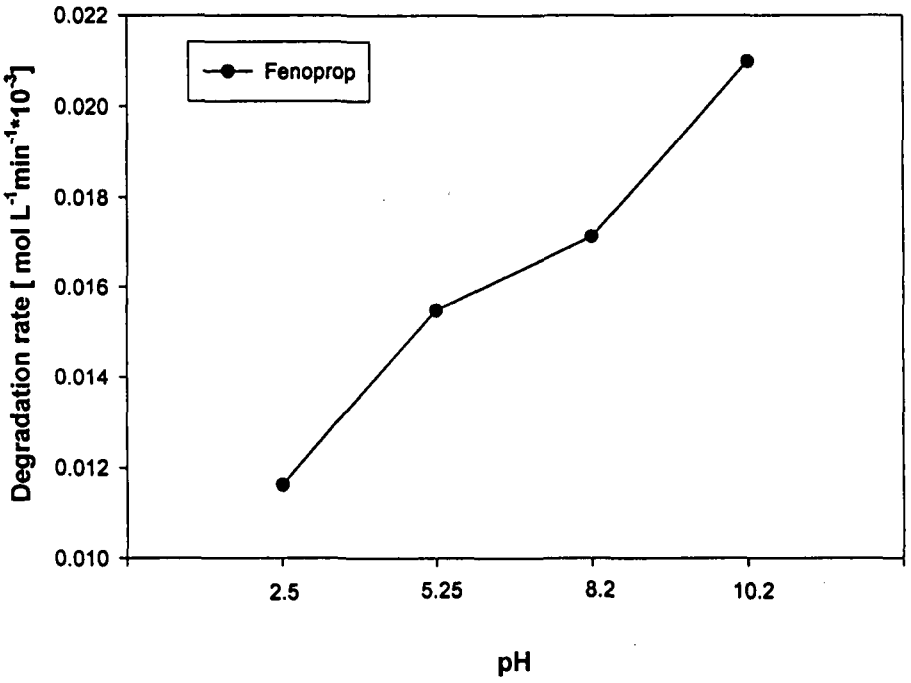


Figure 2.9. Influence of pH on the degradation rate for the decomposition of fenoprop (1).
Experimental conditions: 0.5 mM fenoprop, V=250 mL, photocatalyst: TiO_2 (Degussa P25 1 gL^{-1}), reaction pH (2.5, 5.25, 8.2 and 10.2), irradiation time = 60 min.

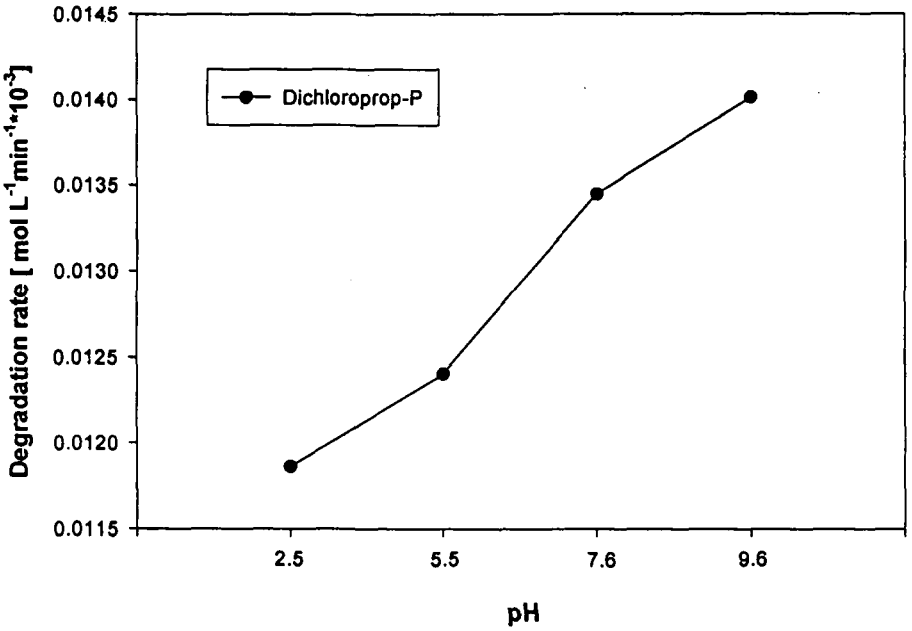


Figure 2.10. Influence of pH on the degradation rate for the decomposition of dichloroprop-P (**2**).
Experimental conditions: 0.4 mM dichloroprop-P, V=250 mL, photocatalyst: TiO_2 (Degussa P25 1 gL^{-1}), reaction pH (2.5, 5.5, 7.6 and 9.6), irradiation time = 60 min.

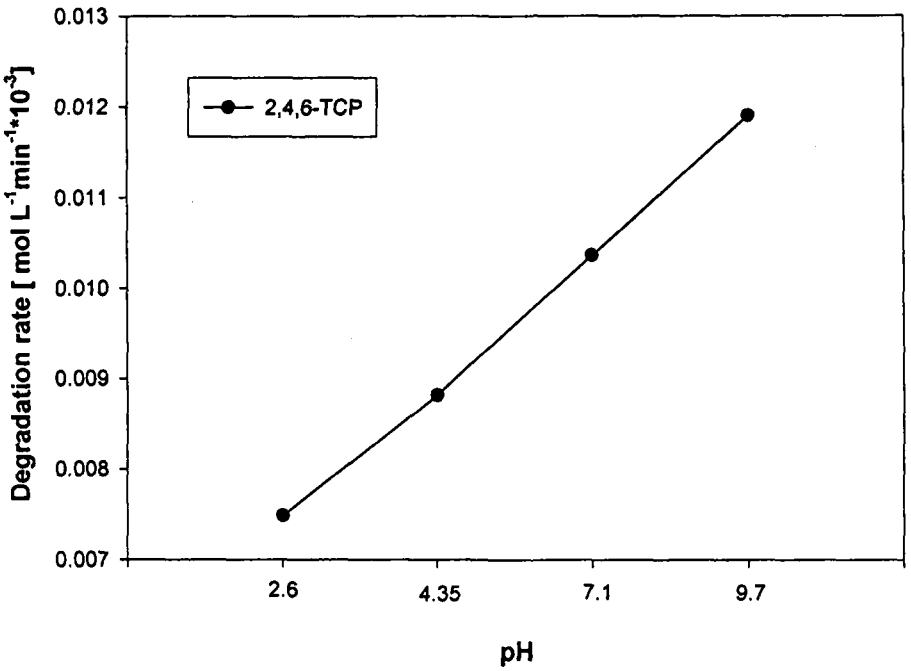


Figure 2.11. Influence of pH on the degradation rate for the decomposition of 2,4,6-TCP (**3**).

Experimental conditions: 0.8 mM 2,4,6-TCP, V=250 mL, photocatalyst: TiO_2 (Degussa P25 1 gL^{-1}), reaction pH (2.6, 4.35, 7.1 and 9.7), irradiation time = 60 min.

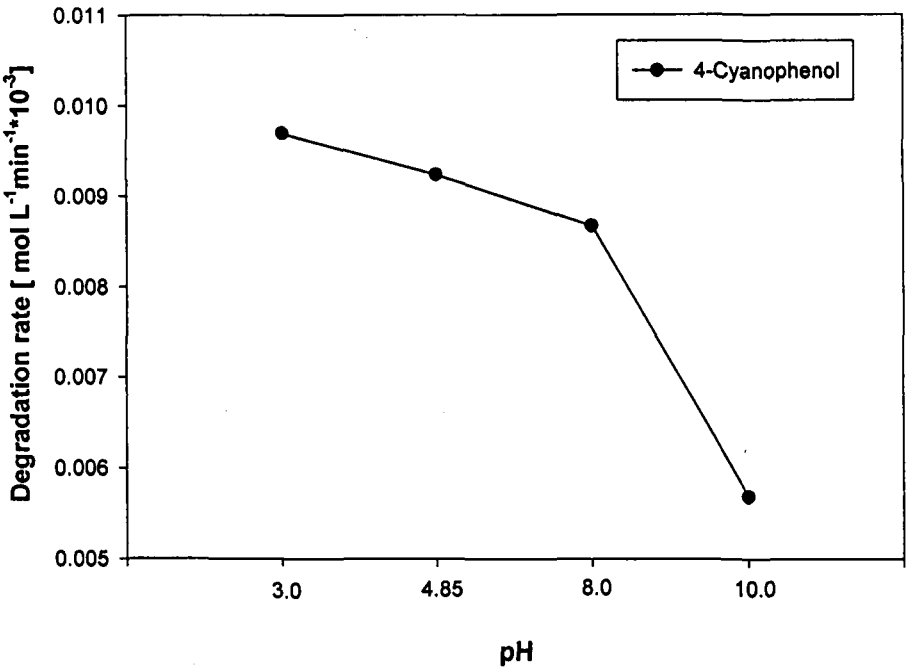


Figure 2.12. Influence of pH on the degradation rate for the decomposition of 4-cyanophenol (**4**).
Experimental conditions: 0.5 mM 4-cyanophenol, V=250 mL, photocatalyst: TiO_2 (Degussa P25 1 gL^{-1}), reaction pH (3.0, 4.85, 8.0 and 10.0), irradiation time = 60 min.

using $1gL^{-1}$ of catalyst. Adsorption of all the compounds were also investigated at their original pH values (8.2 for **1**, 2.5 for **2**, 4.35 for **3**, and 4.85 for **4**) by stirring aqueous solution of compounds, in the dark for 24 h at varying concentration of catalyst such as (0.5, 1, 2, and 3 gL^{-1}). Analysis of the sample after centrifugation indicate some observable loss of the compound only in the case of pesticide derivative **3** at pH 2.6 and 4.35 as shown in Fig. **2.13**.

Our results on the degradation of compounds as a function of pH and adsorption on the surface of catalyst in the dark indicate that the role of adsorption was found to be insignificant in photocatalysis.

All the compounds under investigation can be protonated and deprotonated depending upon the pH of the reaction mixture. It is interesting to note that first three compounds where a chloro group is present in the aromatic ring system are found to degrade faster under alkaline conditions whereas the compound **4** where an electron withdrawing group (CN) is present, the rate was better under acidic conditions. Apparently the structure orientations of the compound at these pH values are favourable for the attack of the reactive species. It is pertinent to mention here that the result obtain for the degradation of compound **3** are in agreement with the earlier study on the effect of pH reported earlier by Tanaka and coworkers.[20]

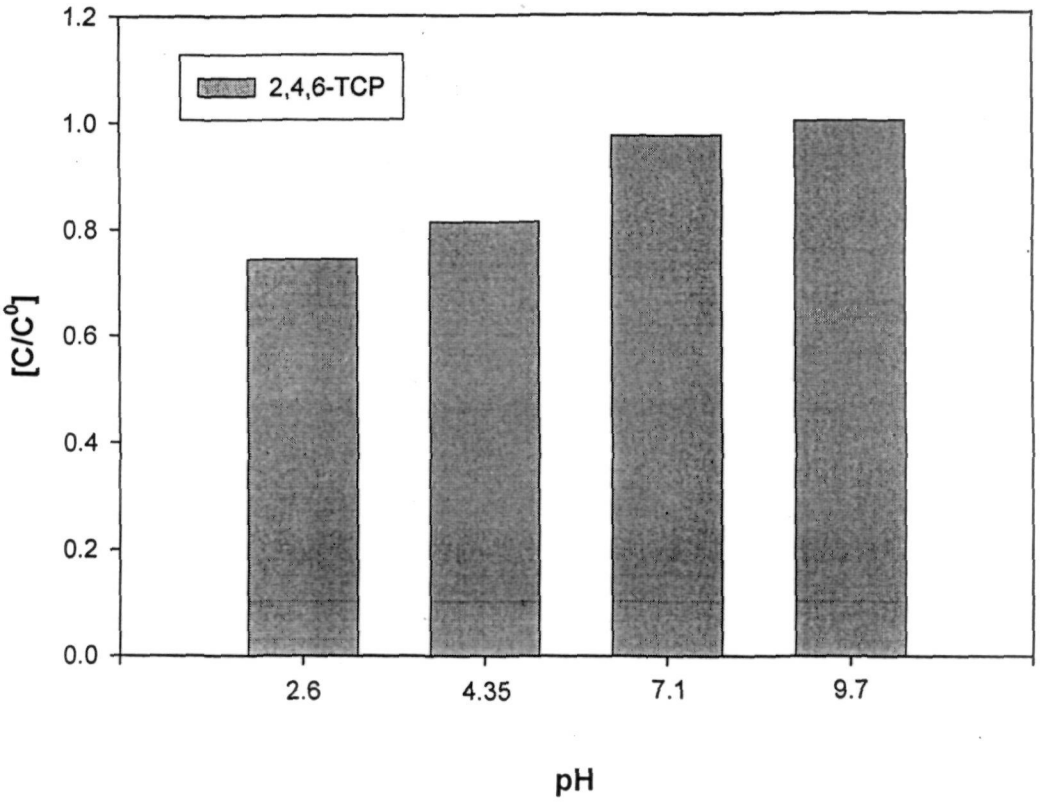


Figure 2.13. Adsorption of 2,4,6 -TCP(**3**) on the surface of photocatalyst by stirring the compound for 24 h
Experimental conditions: 0.8 mM 2,4,6 -TCP, V=20 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (2.6,4.35,7.1 and 9.7), time = 24 h in dark.

2.4.4 Effect of substrate concentration

Effect of initial substrate concentration on the degradation of the model pollutants, **1 - 4** was studied at different concentrations of the compounds. The degradation rate for the decomposition of pesticide derivatives, **1 – 4** as a function of substrate concentration employing Degussa P25 as photocatalyst is shown in Figs. **2.14 – 2.17.**

It was found that the degradation rate for the decomposition of the pesticide derivatives, **1** and **2** increases with the increase in substrate concentration from 0.2 to 0.5 mM. However, in case the of compounds **3** and **4** the rate was found to increase with the increase in substrate concentration from 0.4 to 0.8 mM (for **3**) and 0.2 to 0.4 mM (in case of **4**). A further increase in the initial concentration of the compound lead to decrease in the degradation rate as shown in Figs. **2.16** and **2.17** repectively.

As expected, in the case of compounds, **1** and **2** the rate was found to increase with the increase in substrate concentration followed by leveling off. The unexpected decrease in the degradation rate at higher concentration in **3** and **4** may be due to the fact that increase in substrate concentration can lead to the generation of high concentration of the intermediate products, which may adsorb on the

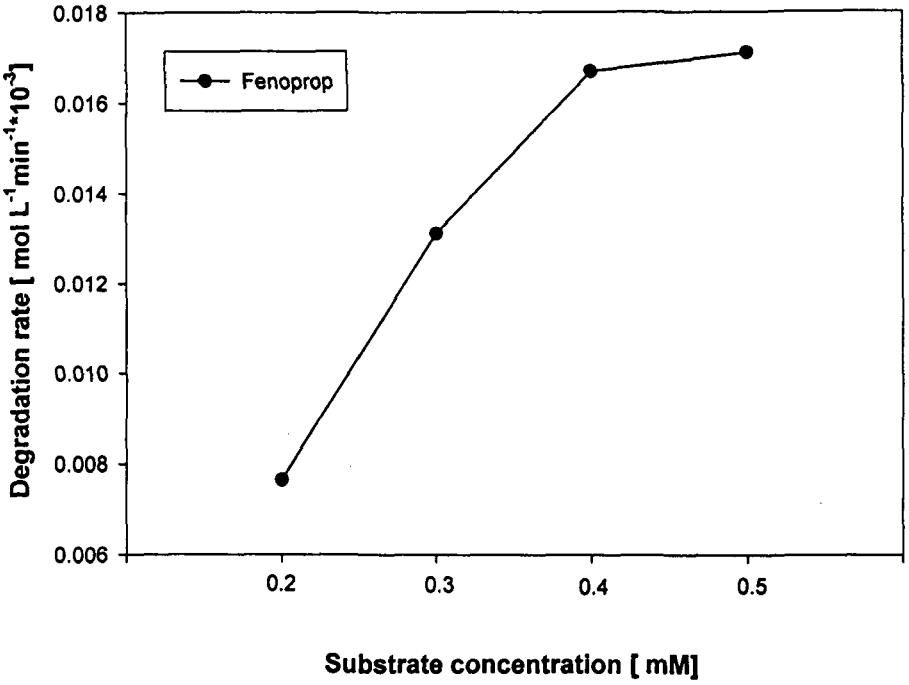


Figure 2.14. Influence of substrate concentration on the degradation rate for the decomposition of fenoprop (1).

Experimental conditions: substrate concentrations (0.2, 0.3, 0.4 and 0.5 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 60 min.

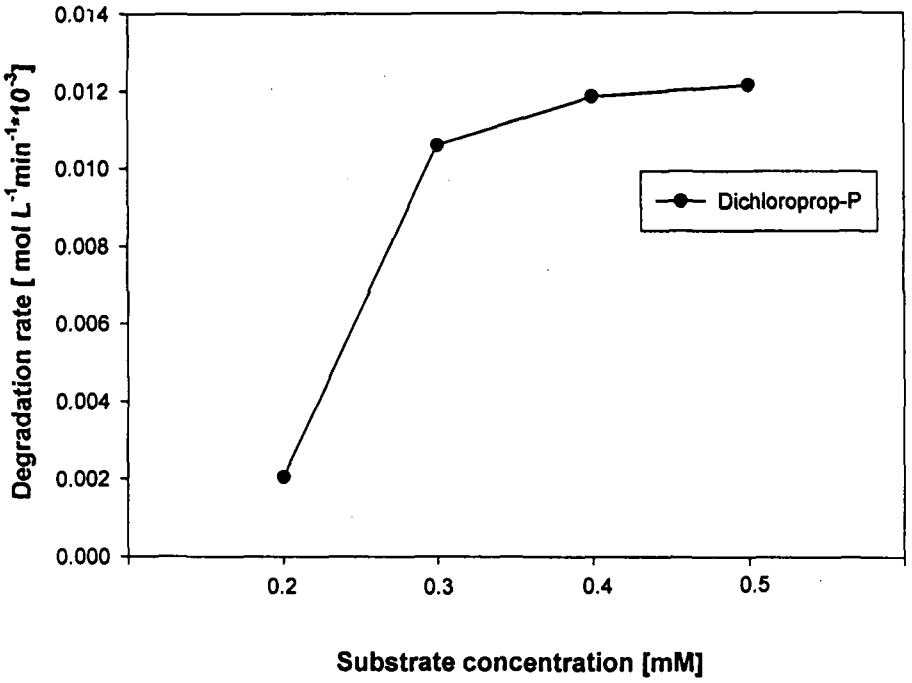


Figure 2.15. Influence of substrate concentration on the degradation rate for the decomposition of dichloroprop-P (**2**).

Experimental conditions: substrate concentrations (0.2, 0.3, 0.4 and 0.5 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 60 min.

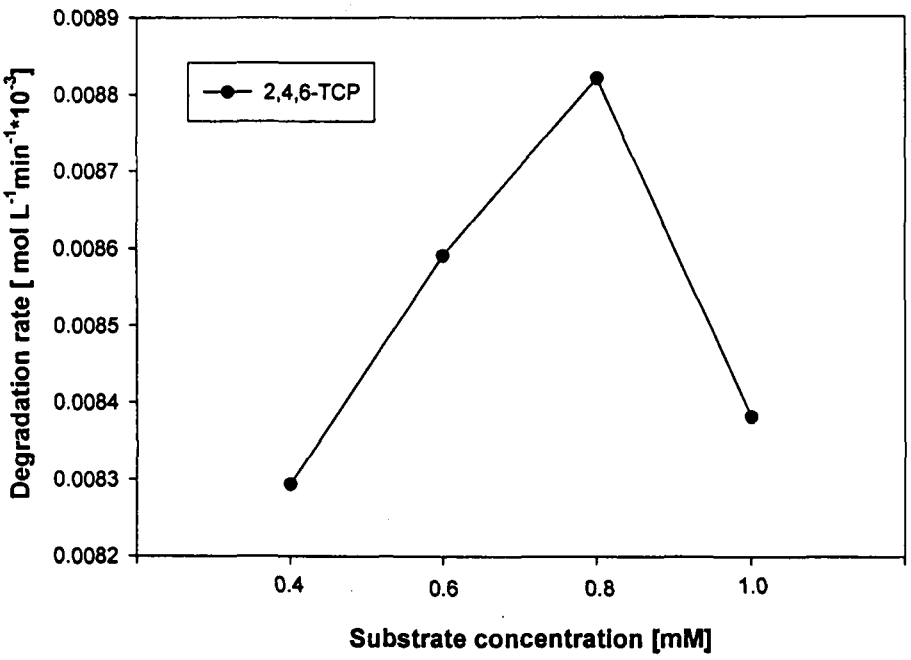


Figure 2.16. Influence of substrate concentration on the degradation rate for the decomposition of 2,4,6-TCP (3).

Experimental conditions: substrate concentrations (0.4, 0.6, 0.8 and 1.0 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 60 min.

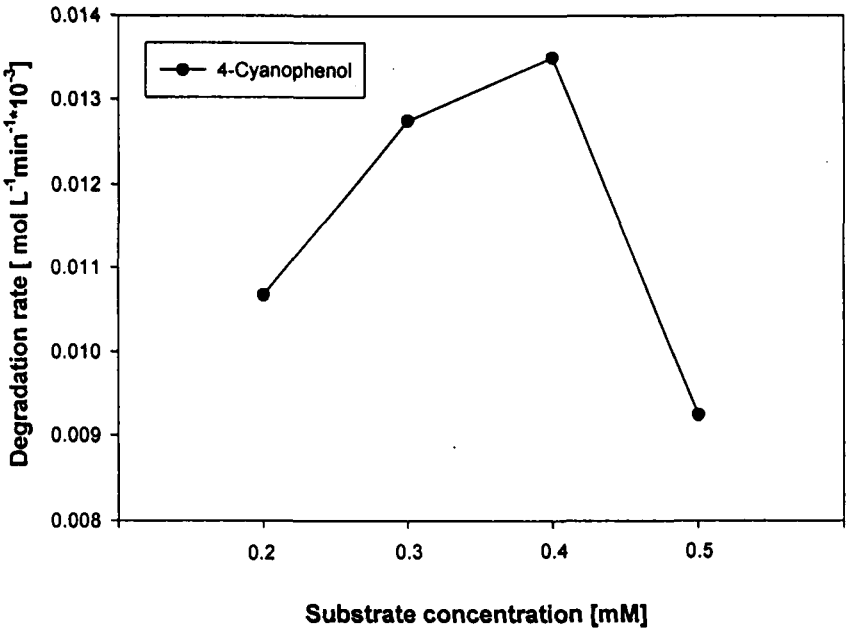


Figure 2.17. Influence of substrate concentration on the degradation rate for the decomposition of 4-cyanophenol (4).

Experimental conditions: substrate concentrations (0.2, 0.3, 0.4 and 0.5 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 60 min.

surface of the catalyst. Hence, a slow diffusion of the intermediate products from the surface of the catalyst may be expected which deactivate or block the catalytic sites of the photocatalyst and consequently, a reduction in the rate of degradation was observed. Secondly, at higher substrate concentration, the increased amount of reactant molecules may also occupy and/or block all the active catalytic sites present on the surface of the photocatalyst and lead to the decrease in the degradation rate. Many workers have reported similar results earlier.[27-29]

2.4.5 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of the pesticide derivatives, **1 – 4** was studied employing different amount of Degussa P25 varying from 0.5 to 3 gL^{-1}. The degradation rate for the decomposition of pesticide derivatives, **1 - 4** as function of different catalyst loading is shown in Figs. **2.18 – 2.21**. The degradation rate for all the compounds under investigations was found to increase markedly on increasing the catalyst loading from 0.5 to 3 gL^{-1}. The reason for increase in degradation rate with the increase in catalyst loading can be interpreted in terms of the fact that as the amount of catalyst increases, the number of photons absorbed and the availability of surface for the adsorption of substrate molecules are

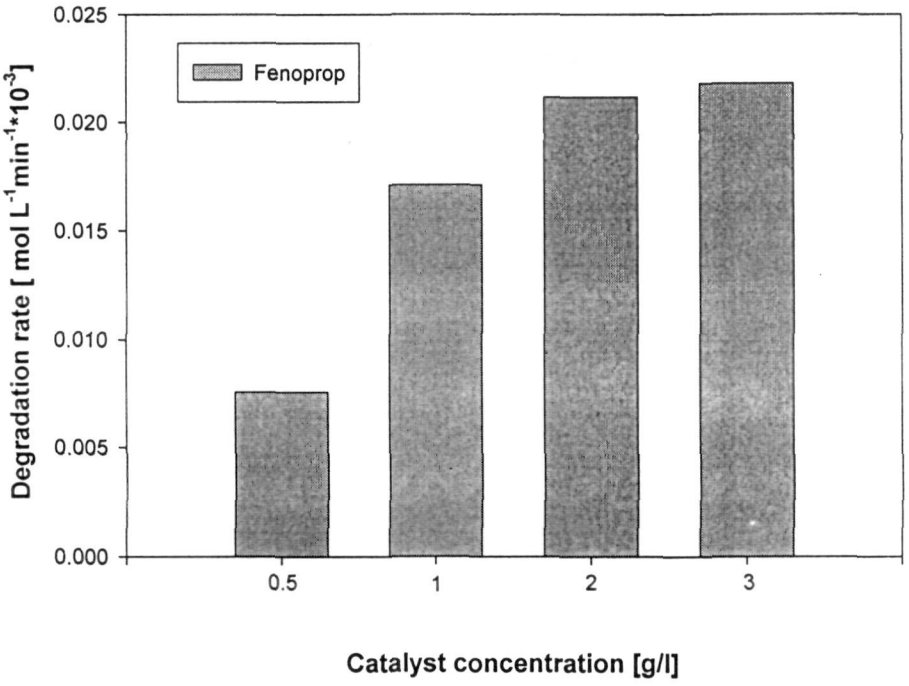


Figure 2.18. Influence of catalyst concentration on the degradation rate for the decomposition of fenoprop (**1**).

Experimental conditions: 0.5mM fenoprop, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 gL^{-1}), irradiation time = 60 min.

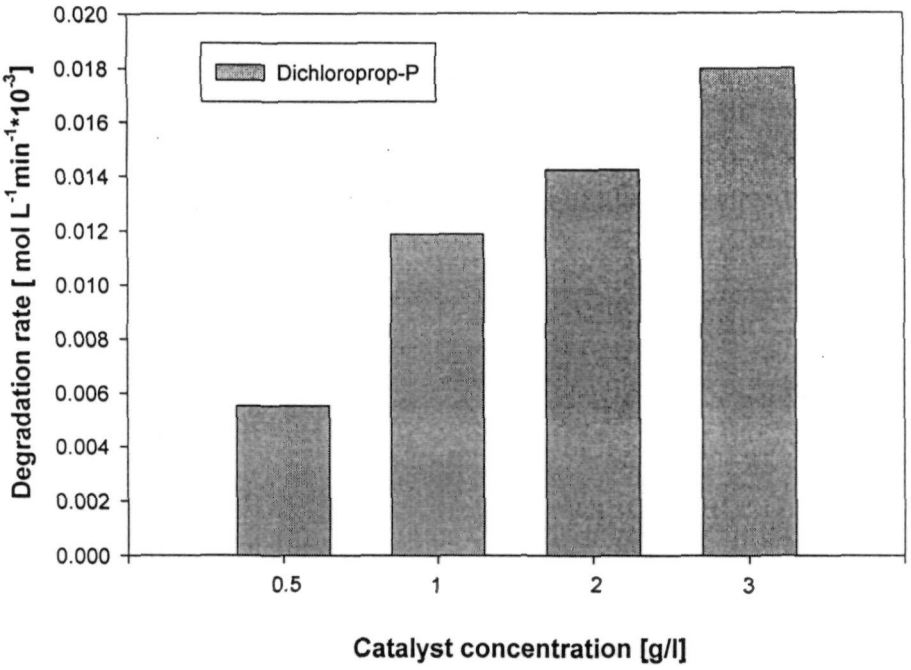


Figure 2.19. Influence of catalyst concentration on the degradation rate for the decomposition of dichloroprop-P (**2**).

Experimental conditions: 0.4 mM dichloroprop-P, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 gL^{-1}), irradiation time = 60 min.

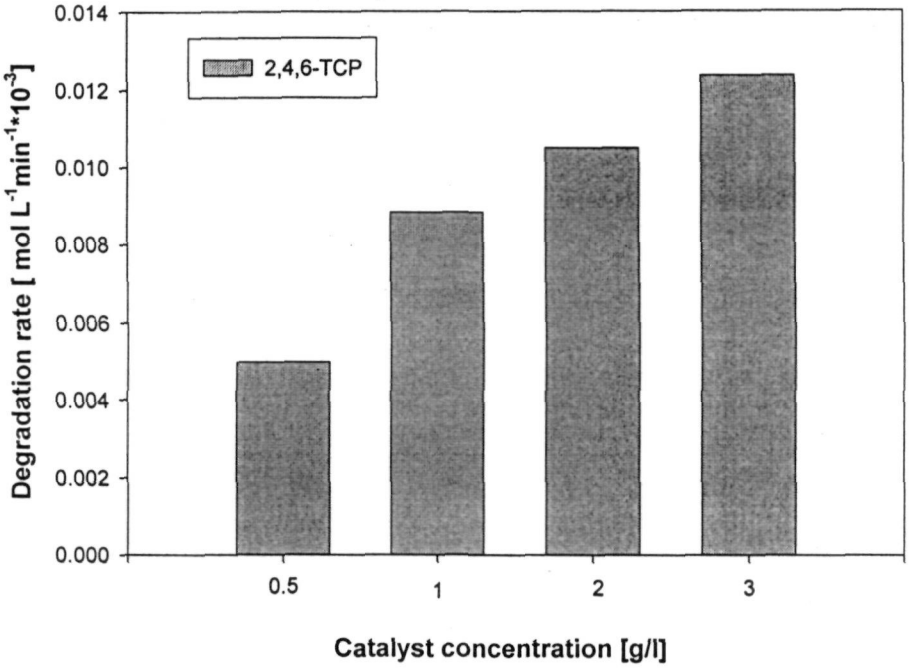


Figure 2.20. Influence of catalyst concentration on the degradation rate for the decomposition of 2,4,6-TCP (**3**).

Experimental conditions: 0.8 mM 2,4,6-TCP, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 gL^{-1}), irradiation time = 60 min.

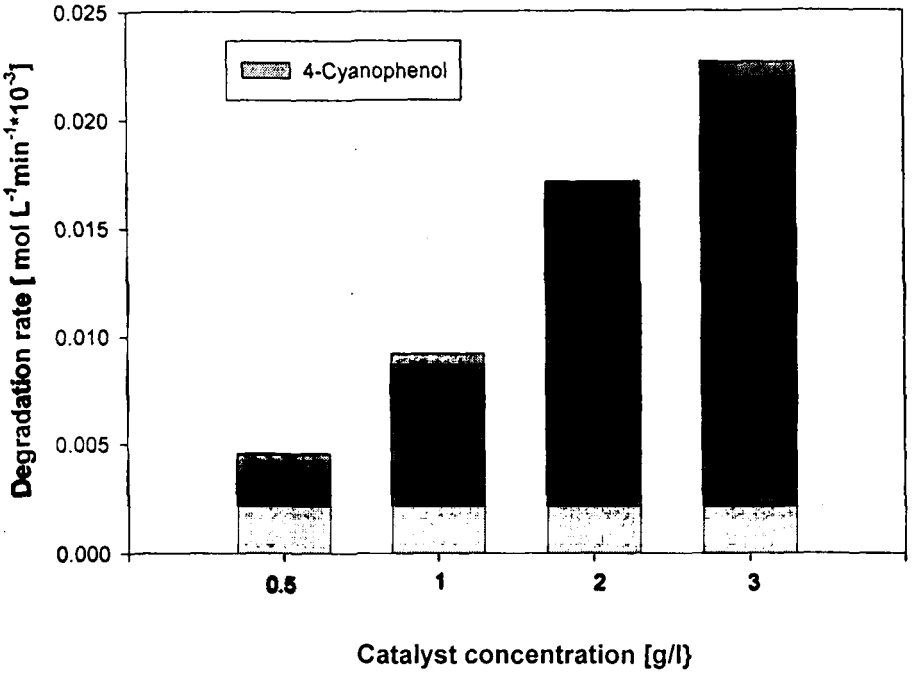


Figure 2.21. Influence of catalyst concentration on the degradation rate for the decomposition of 4-cyanophenol (**4**).

Experimental conditions: 0.5 mM 4-cyanophenol, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 gL^{-1}), irradiation time = 60 min.

increased and consequently, the formation of active species are also increased, this effect lead to higher degradation rate.

2.4.6 Effect of electron acceptors

The effect of electron acceptors such as Hydrogen peroxide, potassium bromate and ammonium persulphate in addition of atmospheric oxygen on the degradation kinetics of the model compounds, **1 - 4** has been investigated in the presence of Degussa P25 as photocatalyst. The degradation rate for the decomposition of compounds **1 - 4** in the presence of different additives is shown in Figs. **2.22–2.25** respectively.

It could be seen from the figures that the addition of bromate ion enhanced the degradation of all the compounds markedly. Whereas the effect of electron acceptors such as H_2O_2 and persulphate ion on the degradation kinetics of compounds **1** and **3** was not pronounced. In contrasts, all the additives showed beneficial effect in the photocatalytic degradation of **2** and the addition of H_2O_2 also enhanced the degradation of **4**, markedly. The effect of electron acceptors on the degradation of organic pollutants via the generation of reactive intermediates and their reduction potential have already been discussed in detail in chapter 1.

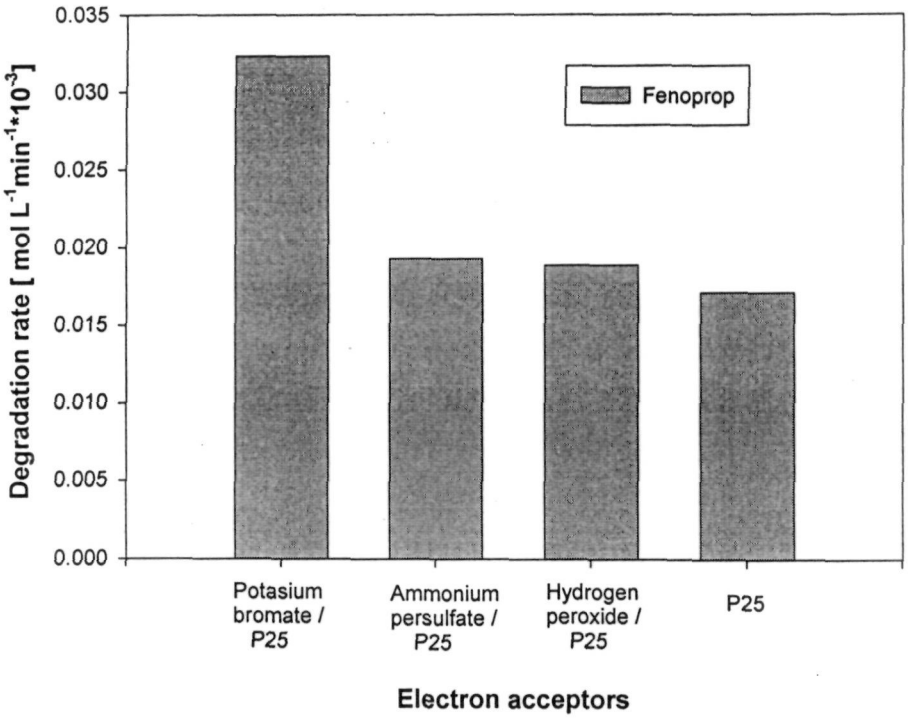


Figure 2.22. Comparison of degradation rate for the decomposition of fenoprop (**1**) in the presence of different electron acceptors.

Experimental conditions: 0.5 mM fenoprop, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM) and H_2O_2 (10 mM), irradiation time = 60 min.

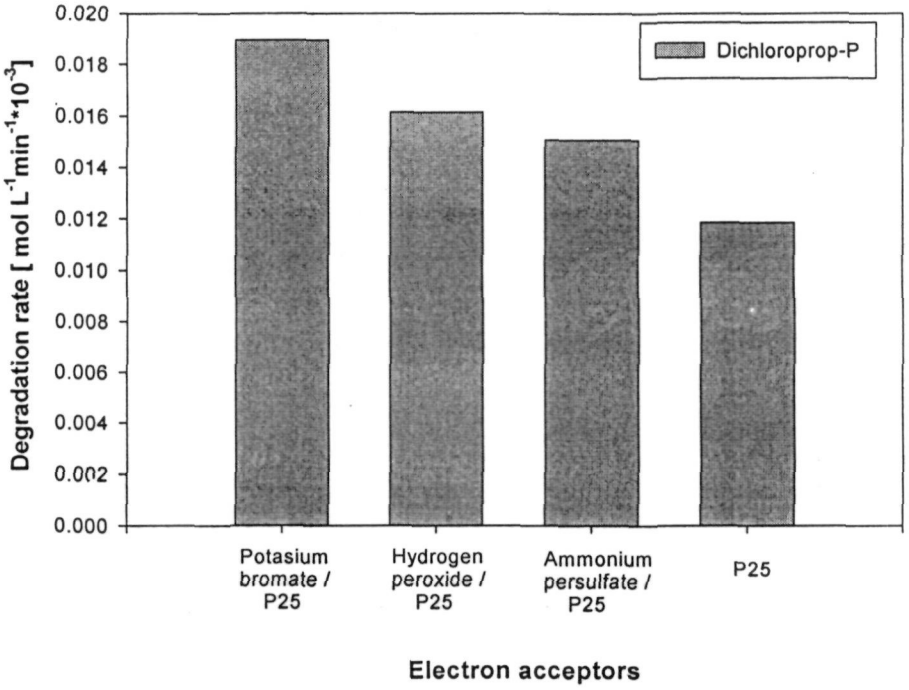


Figure 2.23. Comparison of degradation rate for the decomposition of dichloroprop-P (**2**) in the presence of different electron acceptors.

Experimental conditions: 0.4 mM dichloroprop-P, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 60 min.

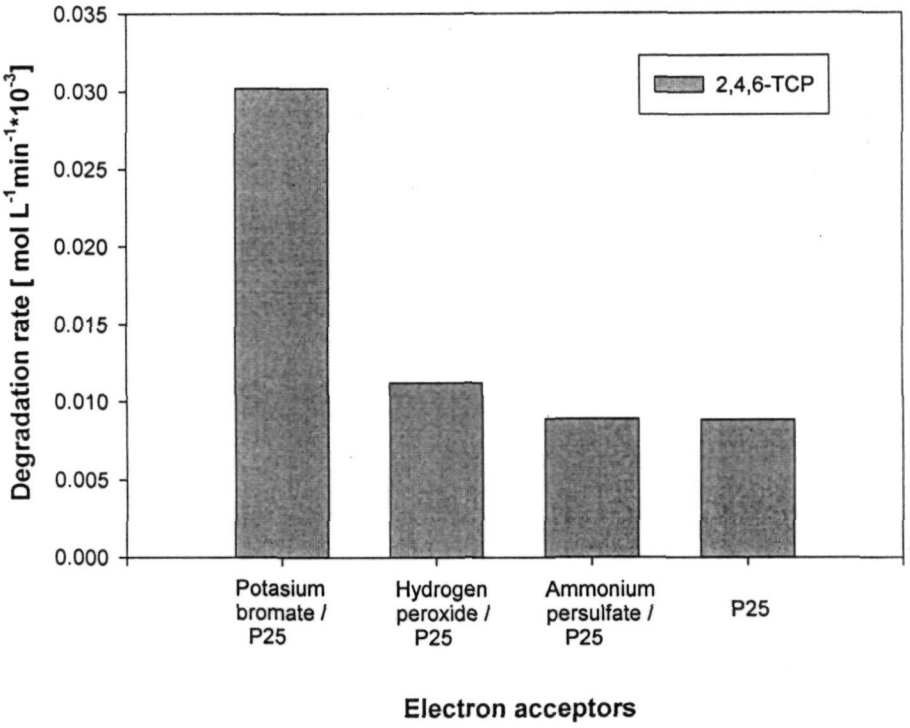


Figure 2.24. Comparison of degradation rate for the decomposition of 2,4,6-TCP (**3**) in the presence of different electron acceptors.

Experimental conditions: 0.8 mM 2,4,6-TCP, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 60 min.

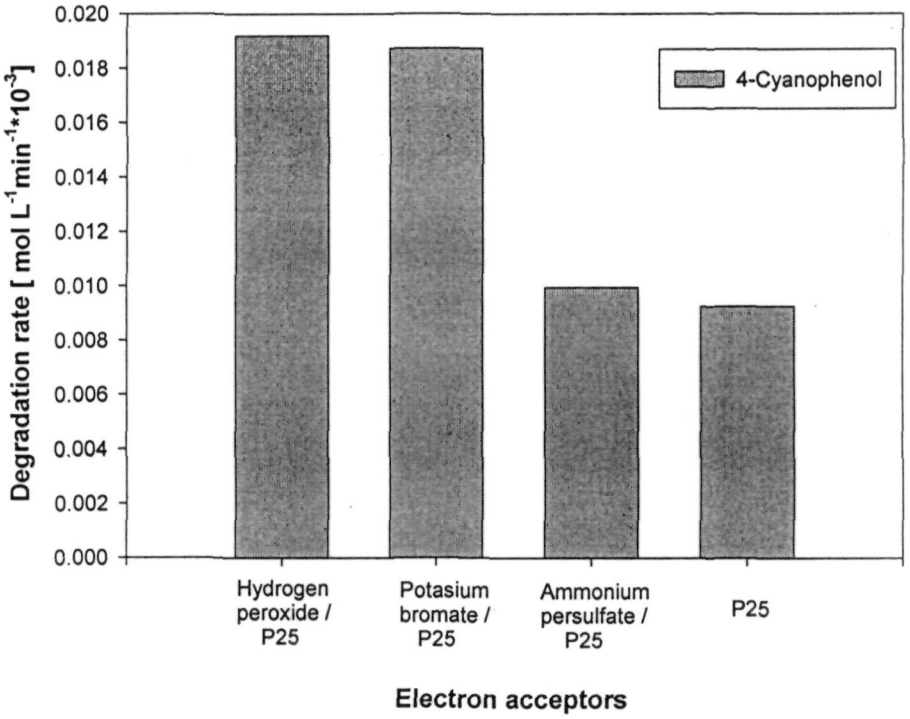


Figure 2.25. Comparison of degradation rate for the decomposition of 4-cyanophenol (**4**) in the presence of different electron acceptors.

Experimental conditions: 0.5 mM 4-cyanophenol, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), $(NH_4)_2S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 60 min.

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Chapter 3

PHOTOCHEMICAL REACTIONS OF THREE SELECTED ORGANIC SYSTEMS, 4-AMINOPHENOL, 2,4-DICHLOROANILINE AND 4-NITROANISOLE IN AQUEOUS SUSPENSIONS OF TITANIUM DIOXIDE[1]

3.1 Abstract

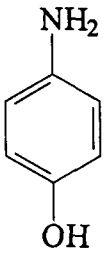
The photochemical reactions of three selected organic systems, such as 4-aminophenol (**1**), 2,4-dichloroaniline (**2**) and 4-nitroanisole (**3**) has been investigated in aqueous suspensions of titanium dioxide in the presence of atmospheric oxygen under a variety of conditions. The degradation was investigated by monitoring the change in substrate concentration employing UV-spectroscopic analysis technique as a function of irradiation time. All the compounds were found to degrade in the presence of TiO_2. The degradation of these compounds were studied under different conditions such as different types of TiO_2, reaction pH, catalyst concentration, substrate concentration and in the presence of electron acceptors such as hydrogen peroxide, ammonium persulphate and potassium bromate besides atmospheric oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 was found to be more efficient for the degradation of model pollutants under investigation.

3.2 Introduction

Environmental pollution is the result of urban-industrial technological revolution and speedy exploitation of every bit of natural resources. The craze of progress in agriculture, industry, transportation and technology is taken as the general criterion of development of any nation. India among these developing countries is an agricultural country where large amount of pesticides are not only produced but also extensively used for the agricultural purposes. These compounds are introduced into the water system through manufacturing units and agricultural runoff. These chemicals are absorbed by plants with water and other nutrients and accumulate in different tissues, which pass through the food chain from one trophic level to other higher trophic level. They may alter the normal physiology of the organism leading to death. In order to tackle this problem, extensive researches are being carried out to develop advanced physico chemical methodologies for the elimination of hazardous chemicals from air, soil and water. Among many processes proposed and/or being developed for the destruction of organic contaminants, biodegradation has received the greatest attention, as it is very cheap. But very often it is unable to reduce the power of the contaminant and is susceptible to toxic compounds that inactivate the waste degrading microorganisms. A promising solution is the oxidation of the pollutants, often upto complete mineralization[2].

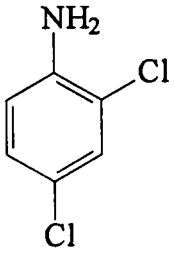
Use of solar energy in solving environmental problems has become very important.[3-9] Semiconductor mediated photochemical reactions of organic and inorganic substrates as a method of treatment of wastewater pollutants is currently attracting considerable attention as reported earlier.[10-15]

The model compound such as 4-aminophenol (**1**) and 2,4-dichloroaniline (**2**) are extensively used as pesticides. 4-Aminophenol is used as a dye for textile, hair, furs and feather. It is also used as photographic developer and chemical intermediate for pharmaceutical and dyes. 2,4-dichloroaniline is used as chemical intermediate in the production of pesticides, plastics, dyes and chlorinated anilines[16]. These organic compounds are highly toxic[17], and are irritating to skin and respiratory system when inhaled. To the best of our knowledge, no effort has been made to study the degradation of these model pollutants under photocatalytic conditions. Therefore, we have undertaken a detailed investigation on the photocatalysed degradation of three selected organic pollutants such as 4-aminophenol (**1**), 2,4-dichloroaniline (**2**) and 4-nitroanisole (**3**) (Chart **3.1**) in aqueous suspensions of TiO_2 under a variety of conditions e.g. reaction pH, substrate and catalyst concentrations, types of photocatalyst and in the presence of electron acceptors, with the aim to determine the



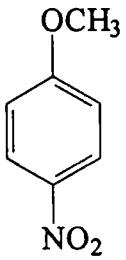
(1)

4- Aminophenol



(2)

2,4-Dichloroaniline



(3)

4-Nitroanisole

Chart 3.1: Chemical Structure and Chemical name

optimal degradation conditions, which is essential for any practical applications.

3.3 Experimental

3.3.1 Reagent and chemicals

Samples of 4-aminophenol (**1,** 98%), 2,4-dichloroaniline (**2,** 99%) and 4-nitroanisole (**3,** 97%) were purchased from Aldrich and used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst, titanium dioxide Degussa P25 (Degussa AG)[18] was used in most of the experiments, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH)[19] and PC500 (Millennium inorganic chemicals)[19] were used for comparative studies. The other chemicals used in this study such as NaOH, HNO_3, $KBrO_3$, H_2O_2 and $(NH_4)_2S_2O_8$ were obtained from Merck.

3.3.2 Procedure

Aqueous solution of compounds, **1 – 3** of desired concentrations were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass was used for irradiation experiments. For irradiation, 250 mL solution of desired concentration of compound was filled into the reactor and required amount of TiO_2 was added. The solution was stirred for at least 10 minutes in the dark

to allow equilibration of the system, so that the loss of compound due to adsorption can be taken into account. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with atmospheric oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (radiant flux $\approx$ 2150 μWcm^{-2}). IR and short wavelength UV radiations were eliminated by water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during irradiation for analysis after centrifugation.

3.3.3 Analysis

The degradation of the model compounds, **1 - 3** was followed by measuring the absorption intensity at their λ_{max} as a function of irradiation time using Shimadzu UV-Vis Spectrophotometer (Model 1601).

3.4 Results and Discussion

3.4.1 Photocatalysis of aqueous suspensions of compounds, 1 - 3 containing TiO_2

Irradiation of aqueous suspensions of desired concentration of model compounds, **1 - 3** in the presence of TiO_2 (Degussa P25, $1gL^{-1}$) with a 125 W medium pressure mercury lamp in the presence of

atmospheric oxygen lead to decrease in absorption intensity as a function of irradiation time. This absorption intensity is used to calculate the concentration using the standard calibration curve. Figs. **3.1 - 3.3** show the change in concentration as a function of time for irradiation of an aqueous suspensions of compounds, **1 – 3** in the presence and absence of photocatalyst.

The curve showing the change in concentration as a function of irradiation time in the presence of photocatalyst for the model compounds, **1 - 3** as shown in Figs. **3.1 - 3.3** can be fitted reasonably well by an exponential decay curve suggesting the first order kinetics. For each experiment, the degradation rate constant was calculated from the plot of the natural logarithm of the concentration of the model compounds as a function of irradiation time.

These rate constants were used to calculate the degradation rate for decomposition of the compounds using formula given below,

$$-d[C]/dt = kc^n \qquad [1]$$

C = concentration, k = rate constant, c = concentration of the pollutant, n = order of reaction.

The degradation rate for the decomposition of the compound for the first order reaction was calculated in terms of mole L^{-1} min^{-1}.

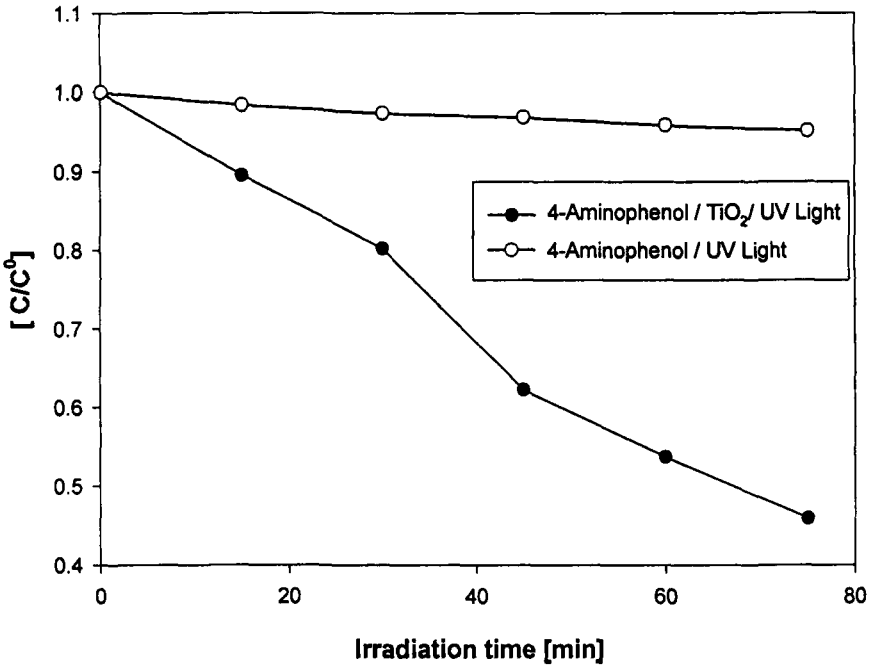


Figure 3.1. Change in concentration as a function of time for irradiation of an aqueous solution of 4-aminophenol (**1**) in the presence and absence of photocatalyst.

Experimental conditions: 0.6 mM 4-aminophenol, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 297 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 75 min.

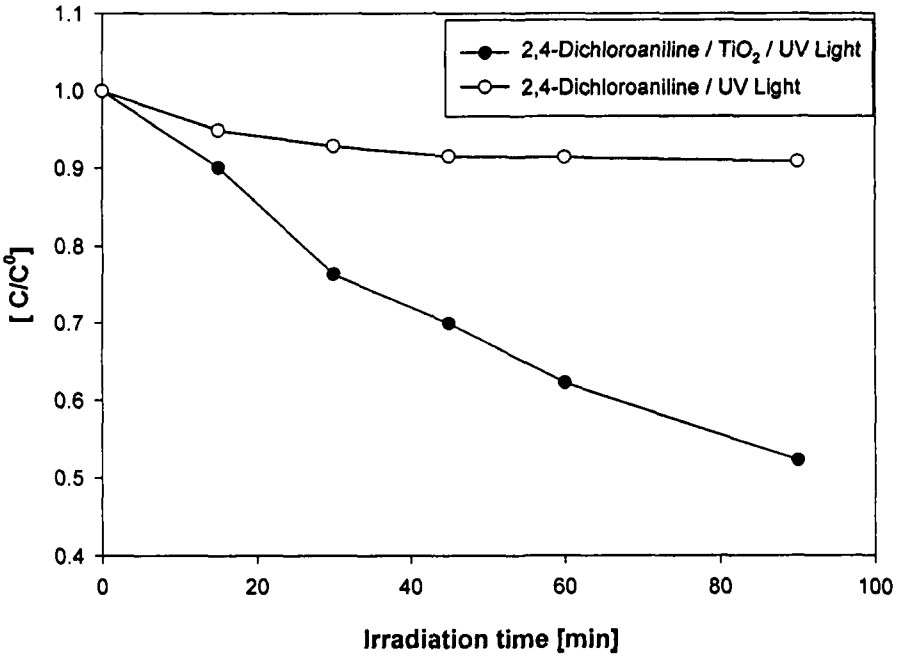


Figure 3.2. Change in concentration as a function of time for irradiation of an aqueous solution of 2,4-dichloroaniline (**2**) in the presence and absence of photocatalyst.

Experimental conditions: 1.0 mM 2,4-dichloroaniline, V=250 mL, photocatalyst: TiO_2 (Degussa P25, $1gL^{-1}$), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 298 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 90 min.

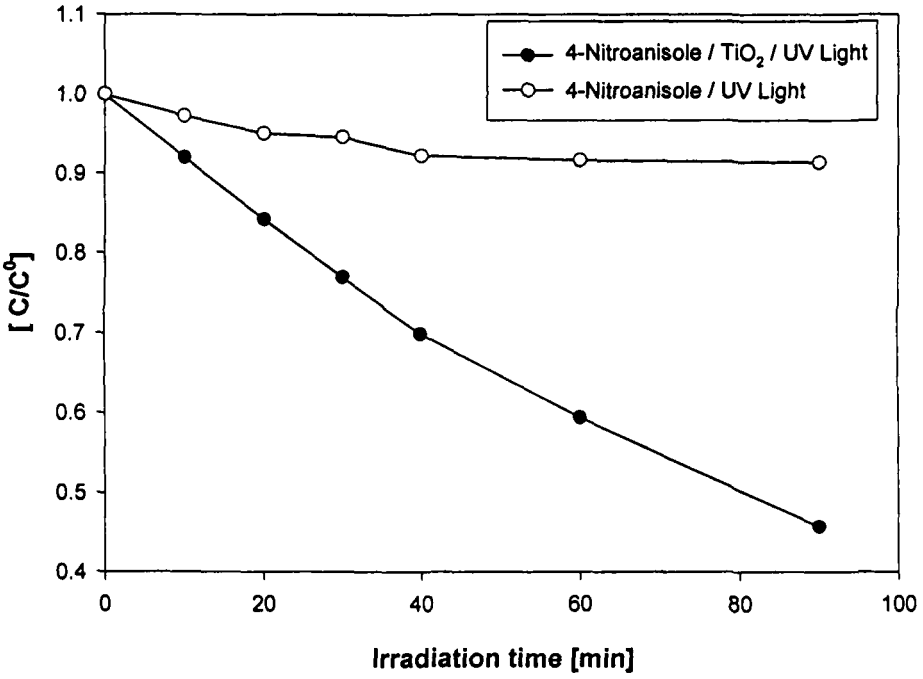


Figure 3.3. Change in concentration as a function of time for irradiation of an aqueous solution of 4-nitroanisole (**3**) in the presence and absence of photocatalyst.

Experimental conditions: 1.0 mM 4-nitroanisole, V=250 mL, photocatalyst: TiO_2 (Degussa P25, $1gL^{-1}$), immersion well photoreactor, 125 W medium pressure Hg lamp, absorbance was followed at 315 nm, continuous atmospheric oxygen purging and stirring, irradiation time = 90 min.

Controlled experiments were carried out in all cases employing unirradiated blank solutions where no observable loss of the compound was seen. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

3.4.2 Comparison of different photocatalysts

The photocatalytic activity of three different commercially available TiO_2 (namely Degussa P25, Hombikat UV100 and Millennium Inorganic PC500) was tested on the degradation of the pollutants under investigation. Figs. **3.4 – 3.6** show the degradation rate for the decomposition of pollutants in the presence of different catalysts. It has been observed that the degradation of model pollutants, **1** - **3** proceed much more rapidly in the presence of Degussa P25.

The details regarding the photocatalytic activity of different TiO_2 samples has already been discussed in chapter **1**. Better efficiency of degradation of Degussa P25 could be attributed on the basis of mixed phase titania as indicated earlier.

In all following experiments, Degussa P25 was used as photocatalyst since this material exhibited the highest over all activity for the degradation of the compounds under investigation in this chapter.

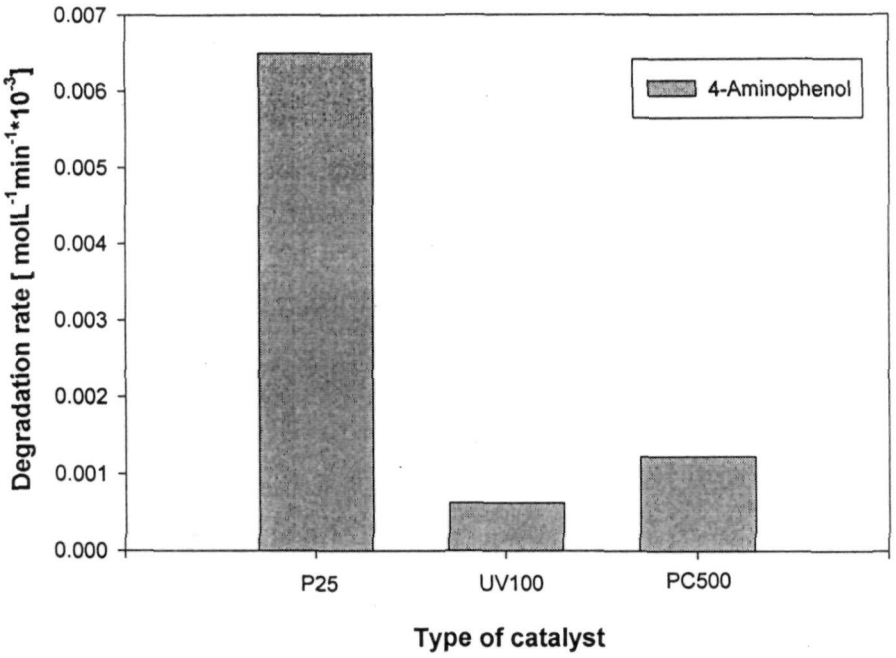


Figure 3.4. Comparison of degradation rate of the decomposition of 4-aminophenol (**1**), in the presence of different type of catalysts.

Experimental conditions: 0.6 mM 4-aminophenol, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC500 (1 gL^{-1}), light source: 125 W medium pressure Hg lamp, immersion well photoreactor, continuous atmospheric oxygen purging and stirring, irradiation time = 75 min.

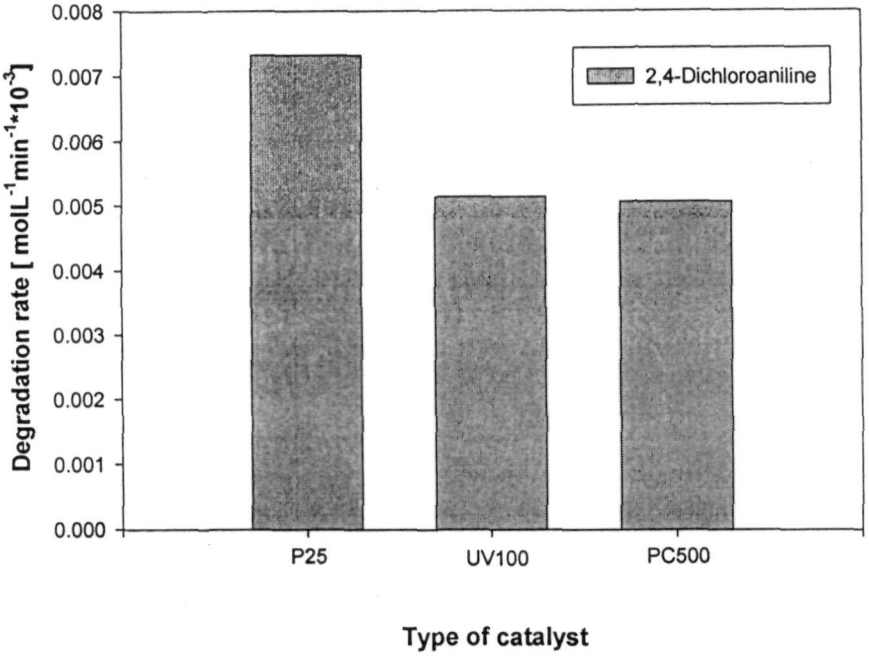


Figure 3.5. Comparison of degradation rate of the decomposition of 2,4-dichloroaniline (**2**), in the presence of different type of catalysts.

Experimental conditions: 1.0 mM 2,4-dichloroaniline, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC500 (1 gL^{-1}), light source: 125 W medium pressure Hg lamp, immersion well photoreactor, continuous atmospheric oxygen purging and stirring, irradiation time = 90 min.

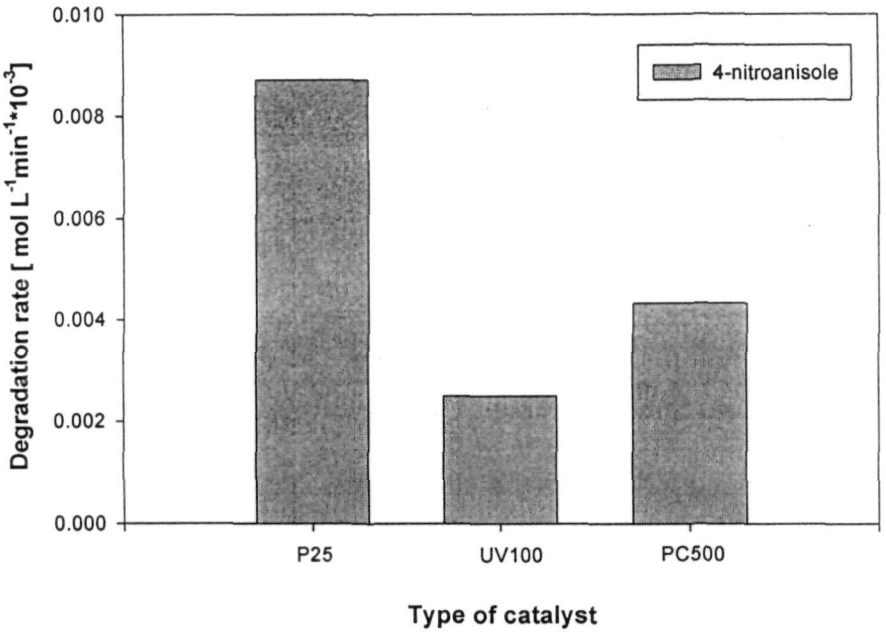


Figure 3.6. Comparison of degradation rate of the decomposition of 4-nitroanisole (**3**), in the presence of different type of catalysts.

Experimental conditions: 1.0 mM 4-nitroanisole, V=250 mL, photocatalyst: TiO_2 Degussa P25, Hombikat UV100 and PC500 (1 gL^{-1}), light source: 125 W medium pressure Hg lamp, immersion well photoreactor, continuous atmospheric oxygen purging and stirring, irradiation time = 90 min.

3.4.3 pH Effect

One of the most important parameter in heterogeneous photocatalysis is the pH of the reaction mixture, since it influences the surface charge properties of the photocatalyst and adsorption behavior of the compound. Therefore, the photocatalytic degradation of the compounds, **1 - 3** was investigated at different pH values.

Employing Degussa P25 as photocatalyst, the degradation of compounds, **1- 3** was studied at different pH values. The degradation rate obtained for the decomposition of compounds, **1- 3** as a function of pH is shown in Figs. **3.7 – 3.9.** It is interesting to note that in the case of compounds **1** and **2**, the rate was found to decrease with increase in pH and highest efficiency was observed at pH 2.6 for **1** and 3.65 for **2**. In contrast in the case of **3** the rate was found to increase with the increase in reaction pH from 2.7 to 9.7 and highest degradation rate was obtained at 9.7.

The adsorption of the compounds, **1 – 3** at different pH values between 2.5 to 9.6 on the surface of the photocatalyst was investigated by stirring the aqueous suspension of compounds in the dark for 24 h using $1gL^{-1}$ of catalyst. Analysis of the sample after centrifugation indicate no observable loss of the compound due to adsorption in the pH range studied.

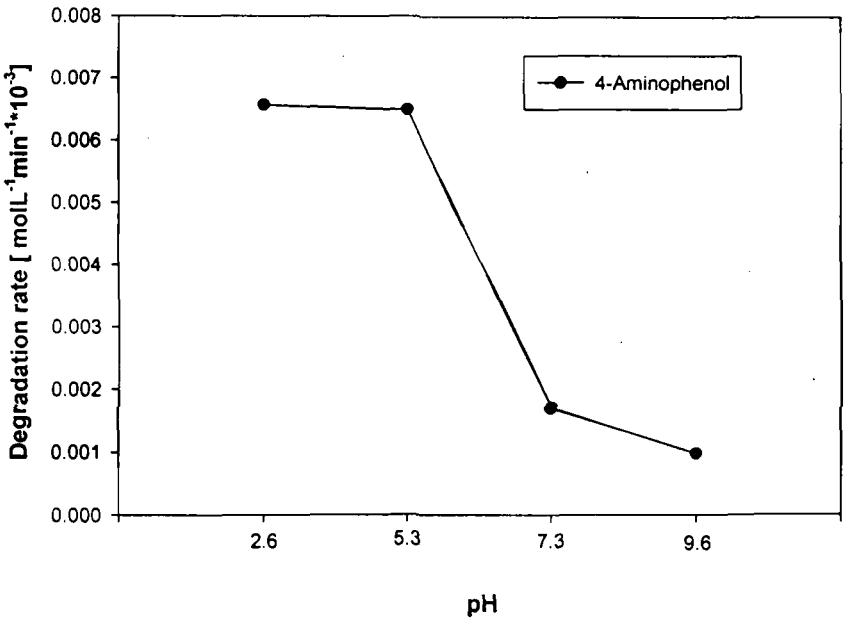


Figure 3.7. Influence of pH on the degradation rate for the decomposition of 4-aminophenol (**1**).
Experimental conditions: 0.6 mM 4-aminophenol, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (2.6, 5.3, 7.3 and 9.5), irradiation time = 75 min.

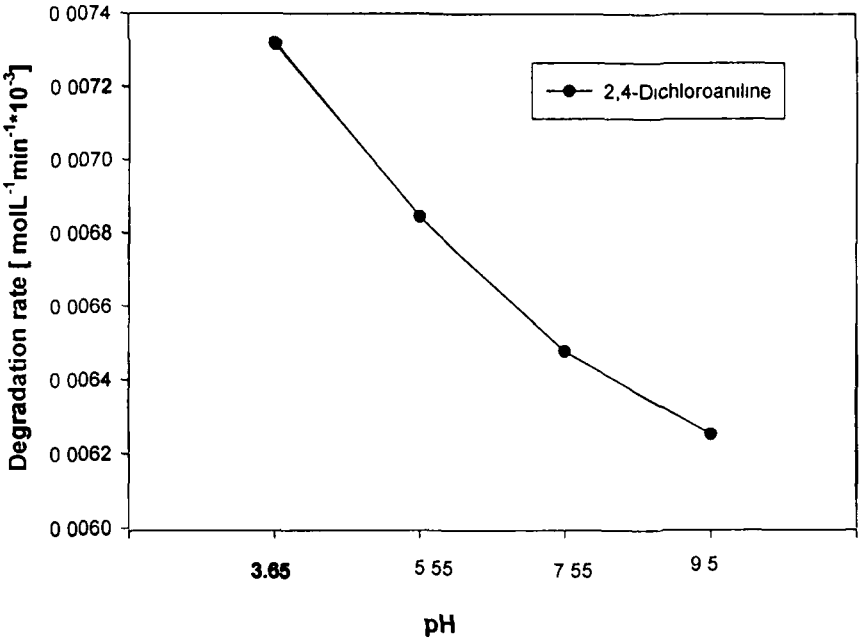


Figure 3.8. Influence of pH on the degradation rate for the decomposition of 2,4-dichloroaniline (**2**).

Experimental conditions: 1.0 mM 2,4-dichloroaniline, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (3.65, 5.55, 7.55 and 9.5), irradiation time = 90 min.

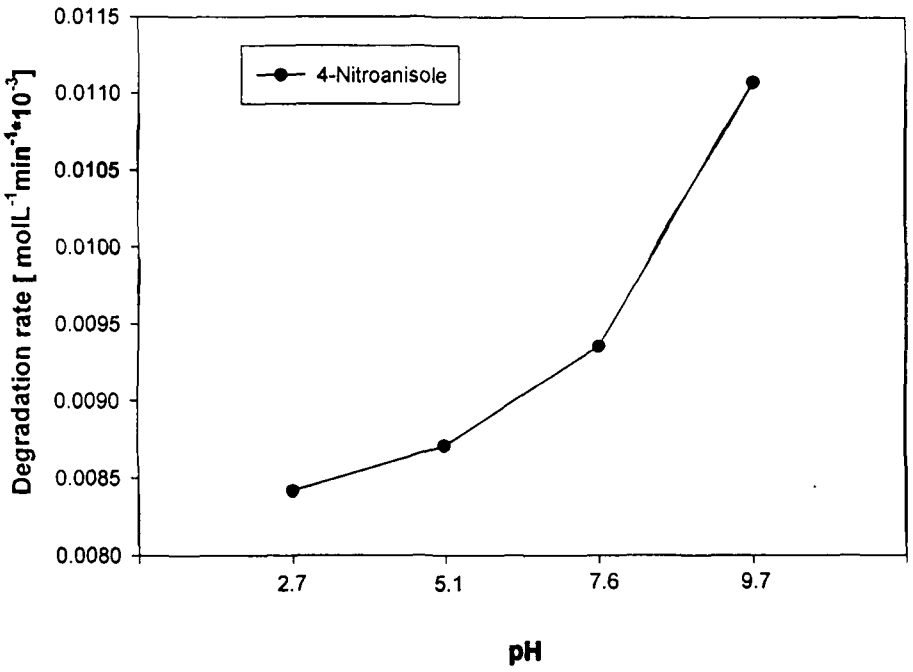


Figure 3.9. Influence of pH on the degradation rate for the decomposition of 4-nitroanisole (**3**).
Experimental conditions: 1.0 mM 4-nitroanisole, V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), reaction pH (2.7, 5.1, 7.6 and 9.7), irradiation time = 90 min.

It is interesting to note that first two compounds, **1** and **2** where amino group is present was found to degrade faster under acidic pH. This may be due to the fact that at this pH value, molecule is in the protonated form and this structure orientation is suitable for the attack of reactive species. The better efficiency for the compound **3** under alkaline condition may due to the more efficient generation of hydroxyl radicals by TiO_2 with increasing concentration of hydroxide ion.

3.4.4 Effect of substrate concentration

Effect of substrate concentration on the degradation of compounds, **1 - 3** was studied at different initial concentrations of the model compounds under investigation. The degradation rate for the decomposition of **1 – 3** as a function of substrate concentration employing Degussa P25 as photocatalyst is shown in Figs. **3.10– 3.12**.

It could be seen from the figure that in the case of **1**, the rate was found to increase continuously with the increase in substrate concentration from 0.4 to 0.7 mM. Whereas, in the case of **2** the rate was found to increase with the increase in substrate concentration from 0.5 to 0.75mM and a further increase in the initial concentration of the compound lead to leveling off in the degradation rate. In contrast in the case of compound, **3** the rate was found to increase with the increase in the initial concentration of the substrate from 0.4 to 0.8 mM

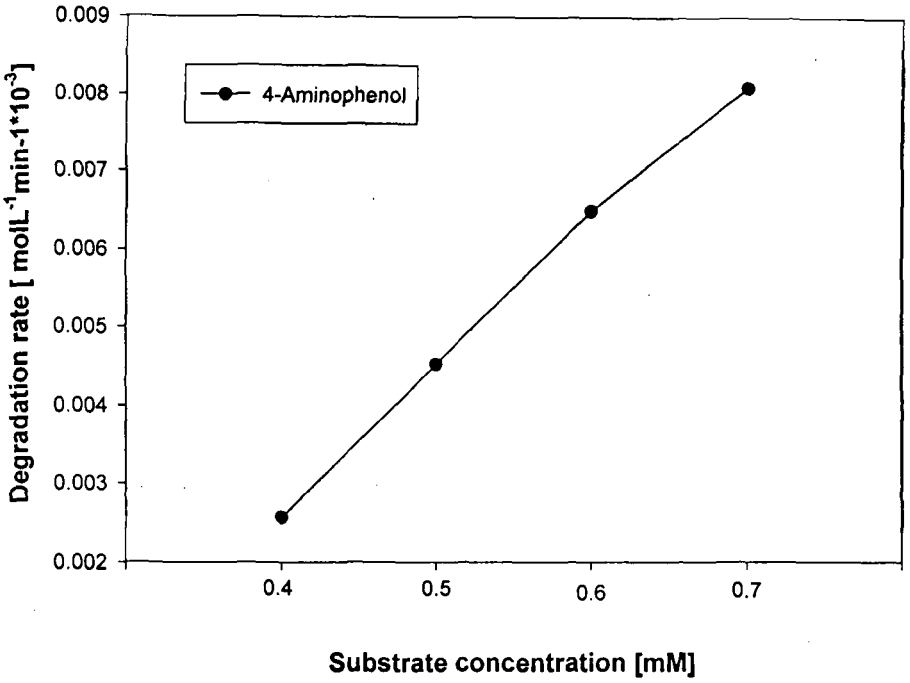


Figure 3.10. Influence of substrate concentration on the degradation rate for the decomposition of 4-aminophenol (**1**).

Experimental conditions: substrate concentrations (0.4, 0.5, 0.6 and 0.7 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time =75 min.

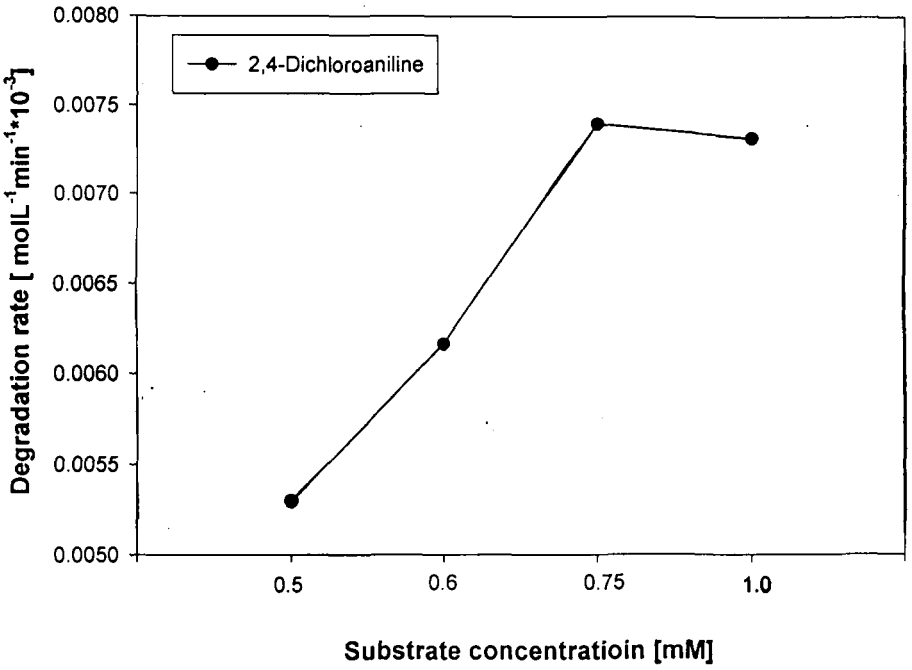


Figure 3.11. Influence of substrate concentration on the degradation rate for the decomposition of 2,4-dichloroaniline (**2**).

Experimental conditions: substrate concentrations (0.5, 0.6, 0.75 and 1.0 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 90 min.

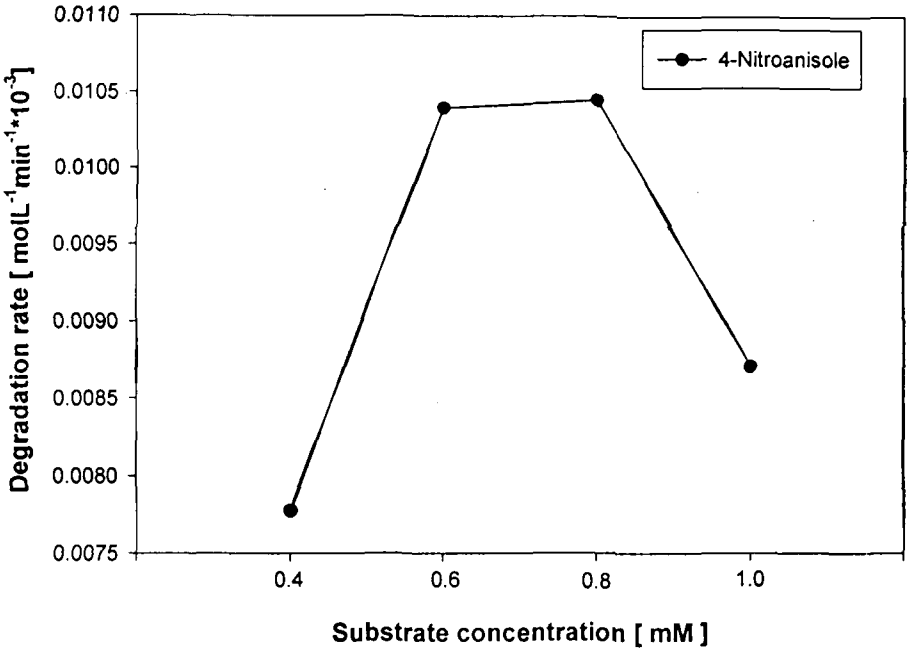


Figure 3.12. Influence of substrate concentration on the degradation rate for the decomposition of 4-nitroanisole (**3**).

Experimental conditions: substrate concentrations (0.4, 0.6, 0.8 and 1.0 mM), V=250 mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), irradiation time = 90 min.

and a decrease in degradation rate was observed in going from 0.8 to 1.0 mM concentration of the compound.

The unexpected decrease in degradation rate at higher initial substrate concentration could be explained on the basis of two reasons. Firstly, increase in substrate concentration can lead to the generation of high concentration of the intermediate products, which may adsorb on the surface of the catalyst. Hence, a slow diffusion of the intermediate products from the surface of the catalyst may be expected which deactivate or block the catalytic sites of the photocatalyst and consequently, a reduction in the rate of degradation was observed. Secondly, at higher substrate concentration, the increased amount of reactant molecules may also occupy and/or block all the active catalytic sites present on the surface of the photocatalyst and lead to the decrease in the degradation rate. Many workers have reported similar results earlier.[20-22]

3.4.5 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of model compounds, **1** - **3** under investigation was studied employing different amounts of Degussa P25 varying from 0.5 to 3 gL^{-1}. The degradation rate for the decomposition of model compounds, **1** - **3** as function of different catalyst loading is shown in Figs. **3.13 – 3.15**.

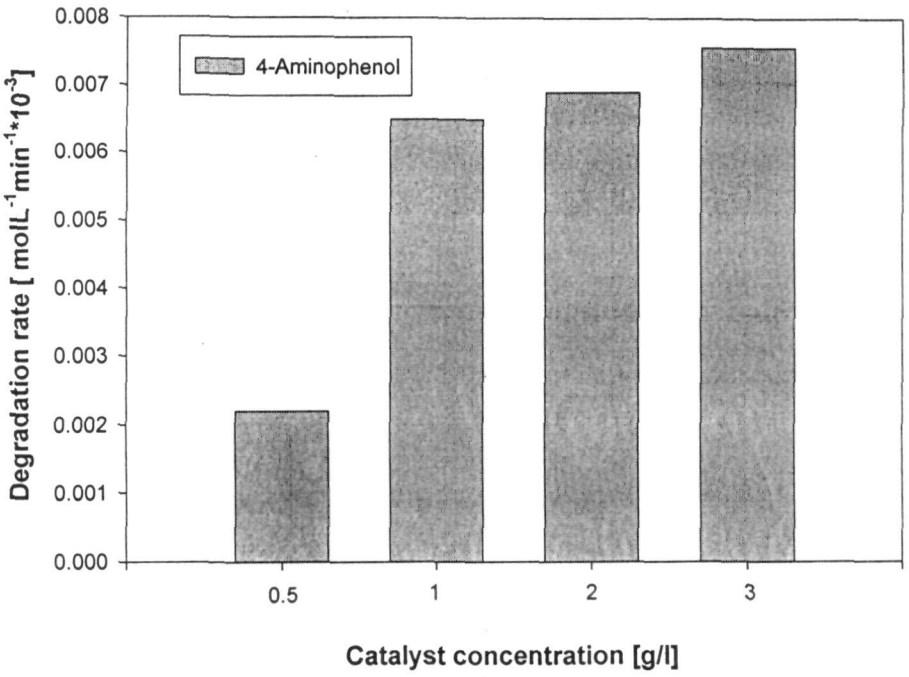


Figure 3.13. Influence of catalyst concentration on the degradation rate for the decomposition of 4-aminophenol (**1**).

Experimental conditions: 0.6 mM 4-aminophenol, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 gL^{-1}), irradiation time = 75 min.

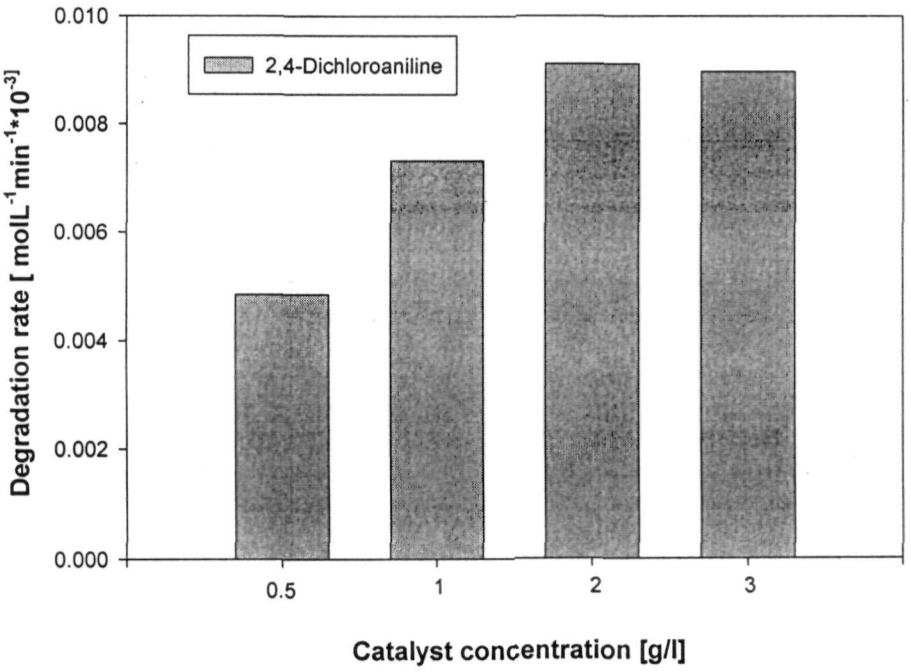


Figure 3.14. Influence of catalyst concentration on the degradation rate for the decomposition of 2,4-dichloroaniline (**2**).

Experimental conditions: 1.0 mM 2,4-dichloroaniline, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 gL^{-1}), irradiation time = 90 min.

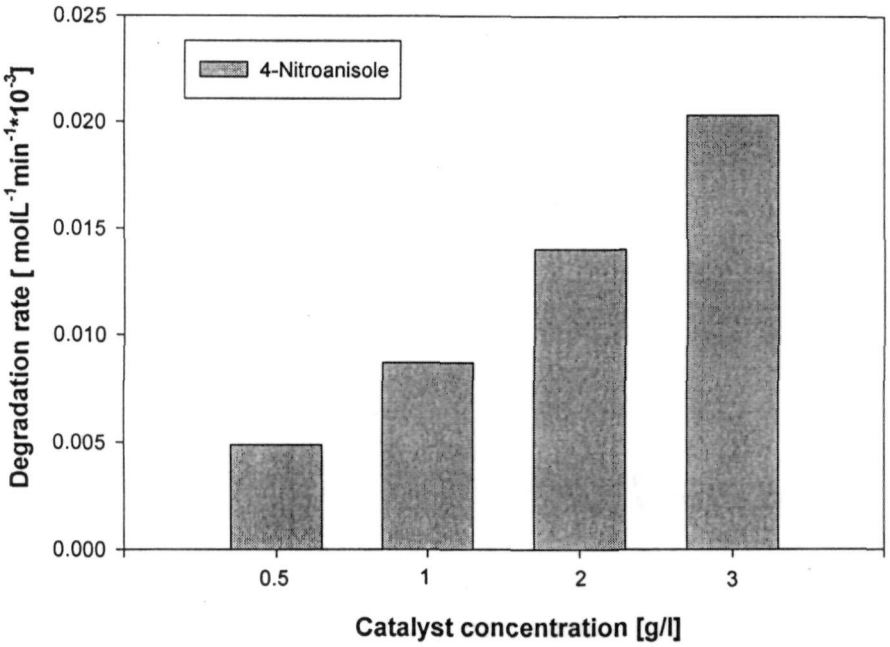


Figure 3.15. Influence of catalyst concentration on the degradation rate for the decomposition of 4-nitroanisole (**3**).

Experimental conditions: 1.0 mM 4-nitroanisole, V=250 mL, photocatalyst: TiO_2 Degussa P25 (0.5, 1.0, 2.0 and 3.0 gL^{-1}), irradiation time = 90 min.

It is interesting to note that in the case of compounds **1** and **3**, the rate was found to increase continuously with the increase in catalyst loading from 0.5 to 3 gL^{-1}. In contrast in the case of **2**, the rate was found to increase with the increase in catalyst loading from 0.5 to 2 gL^{-1} and a further increase in catalyst loading from 2 to 3 gL^{-1} lead to the leveling off of the rate for the decomposition of the compound as shown in Fig. **3.14**.

This can be interpreted in terms of the fact that as the availability of surface for the adsorption of substrate molecules are increased, consequently, the formation of active species are also increased, this effect leads to higher degradation rate.

3.4.6 Effect of electron acceptors

The effect of electron acceptors such as Hydrogen peroxide, potassium bromate and ammonium persulphate in addition to atmospheric oxygen on the degradation kinetics of the model compounds, **1 - 3** has been investigated in the presence of Degussa P25 as photocatalyst. The degradation rate for decomposition of compounds, **1 - 3** in the presence of different electron acceptors is shown in Figs. **3.16 – 3.18** respectively.

In the case of compound **1**, the addition of electron acceptors did not show any pronounced effect on the enhancement of the rate

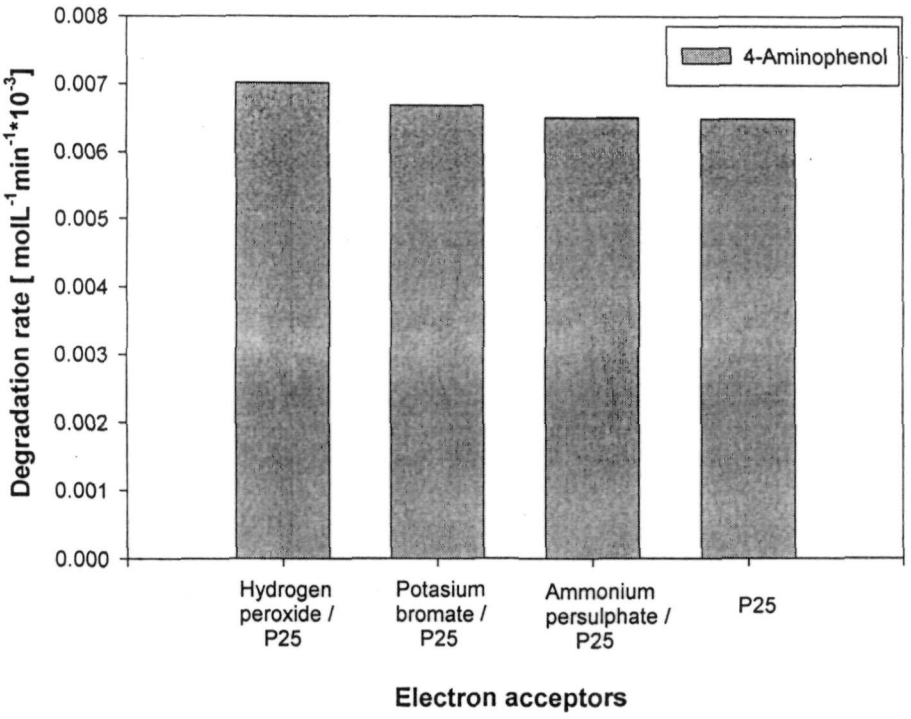


Figure 3.16. Comparison of degradation rate for the decomposition of 4-aminophenol (**1**) in the presence of different electron acceptors.

Experimental conditions: 0.6 mM 4-aminophenol, V=250mL, photocatalyst: TiO_2 (Degussa P25, $1gL^{-1}$), electron acceptors: $KBrO_3$ (3mM), $NH_4S_2O_8$ (3 mM), H_2O_2 (10 mM) irradiation time = 75 min.

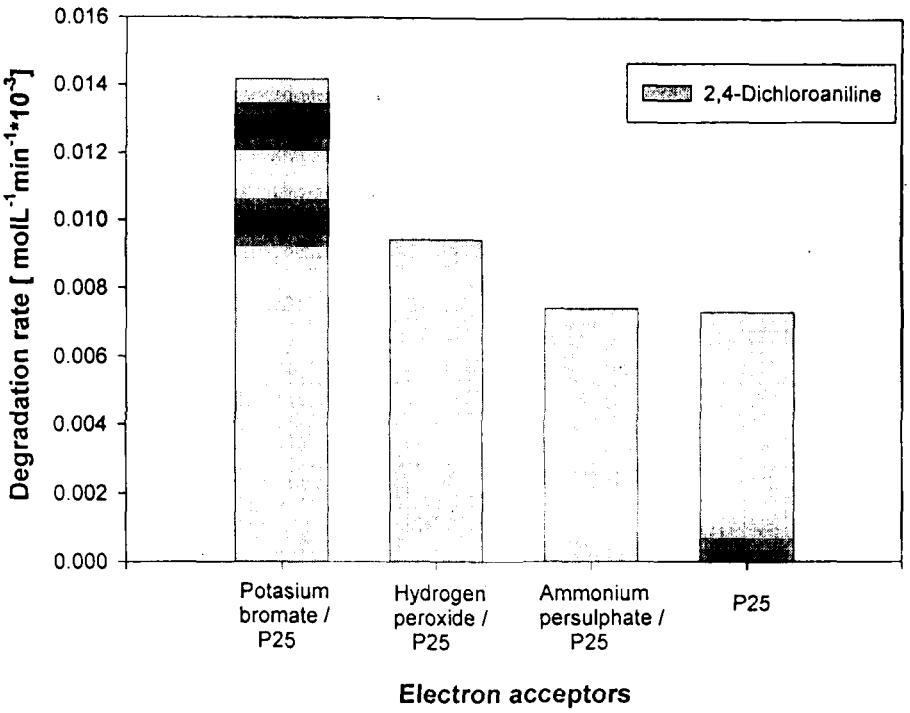


Figure 3.17. Comparison of degradation rate for the decomposition of 2,4-dichloroaniline (**2**) in the presence of different electron acceptors.
Experimental conditions: 1.0 mM 2,4-dichloroaniline, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), $NH_4S_2O_8$ (3 mM), H_2O_2 (10 mM), irradiation time = 90 min.

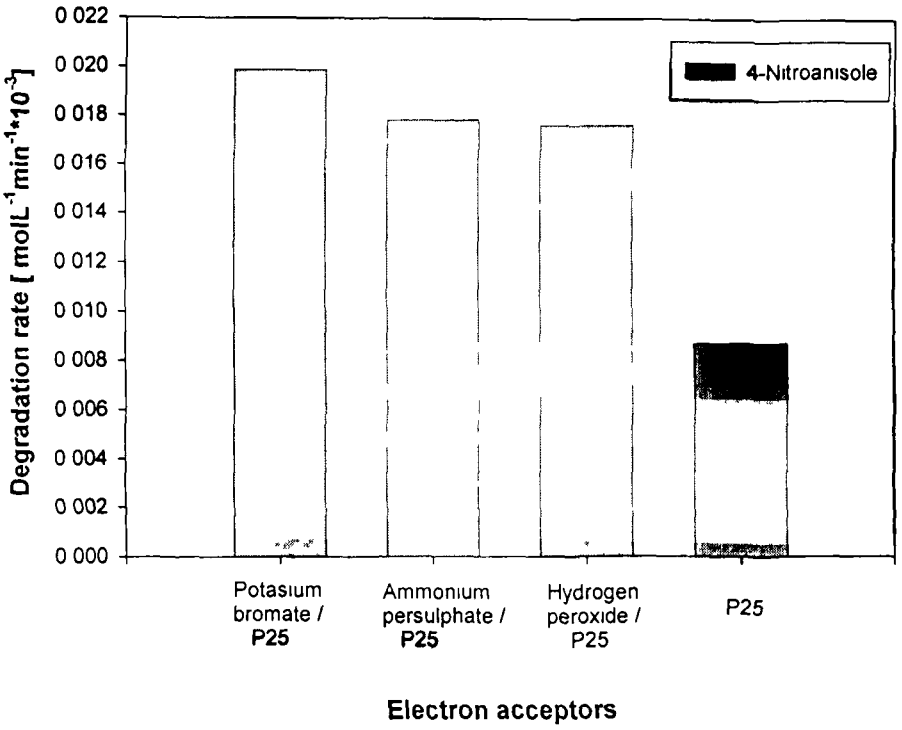


Figure 3.18. Comparison of degradation rate for the decomposition of 4-nitroanisole (**3**) in the presence of different electron acceptors.

Experimental conditions: 1.0 mM 4-nitroanisole, V=250mL, photocatalyst: TiO_2 (Degussa P25, 1 gL^{-1}), electron acceptors: $KBrO_3$ (3 mM), $NH_4S_2O_8$ (3 mM), and H_2O_2 (10 mM), irradiation time = 90 min.

for the decomposition of the compound. In contrast in the case of **2** the addition of electron acceptors such as potassium bromate and hydrogen peroxide showed enhanced degradation rate. On the otherhand, all additives showed beneficial effect on the degradation rate for the decomposition of compound **3**.

The details regarding the effect of electron acceptors on the enhancement of the efficiency on the degradation rate for the organic pollutants in terms of reactions producing reactive species and their reduction potentials have already been indicated in chapter **1**.

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19. The photocatalyst PC500 and Hombikat UV100 was a gift sample from Dr. D. W. Bahnemann from The Institut fuer Technische Chemie Universitat Hannover, Germany.

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Chapter 4

PHOTOCHEMICAL REACTIONS OF FEW SELECTED ORGANIC SYSTEMS IN AQUEOUS SUSPENSIONS OF TITANIUM DIOXIDE[1,2]

4.1 Abstract

The photocatalysed reaction of few selected organic systems, namely 2, 2′-dinitrobiphenyl (**1**), N, N-dimethyl-4-nitrosoaniline (**2**), 4-(dimethylamino)benzaldehyde (**3**), Phthalaldehyde (**4**) and tetramethyl-1,4-benzoquinone (**5**) has been investigated in acetonitrile/water mixture in the presence of titanium dioxide and oxygen. An attempt was made to identify the products formed during the photooxidation process through GC/MS analysis technique. The photolysis of 2, 2′ dinitrobiphenyl (**1**) in the presence of TiO_2 in acetonitrile/water mixture for 11 h lead to the formation of 2-hydroxy-2′-nitro biphenyl (**6**), 2, 2′ dihydroxy biphenyl (**7**) and 2-aminobiphenyl (**11**). The photolysis of N, N- dimethyl-4-nitrosoaniline (**2**) under analogous condition followed by GC/MS analysis of the irradiated mixture gave rise to N, N- dimethyl-4-nitroaniline (**14**) and N, N dimethyl-1,4-benzenediamine (**15**). Photolysis of 4-(dimethylamino)benzaldehyde (**3**) yielded demethylated product (**17**) as the only identified product. The irradiation of Phthalaldehyde (4), on the other hand, led to the

formation of two products such as 1(3H)-isobenzofuranone (**23**) and 2-formyl-benzoic acid (**20**). Two intermediate products, namely tetramethyl hydroquinone (**34**) and 2, 5-furandione, 3, 4-dimethyl- (**33**) have been identified in case of tetramethyl-1,4- benzoquinone (**5**). The products were characterised by comparing the molecular ion and mass fragmentation pattern of the products with those reported in the GC/MS library. A probable mechanism for the formation of the products has been proposed.

4.2. Introduction

The photocatalysed reaction of organic compounds in the presence of semiconductor such as TiO_2 has become a subject of serious study as it shows promise in becoming a viable commercial technology for the wastewater treatment[3-8]. Among all explorations for potential application, the most active area of the past decade has been the photocatalysis for environmental remediation due to the emerging concern for the environment and the successful destruction of a wide range of pollutants on illuminated semiconductor particles such as TiO_2[9].

Generally, semiconductor-mediated photocatalysis involves photoexcitation that causes charge separation in semiconductor particles followed by simultaneous oxidation and reduction of the adsorbed organic substrates. The lifetime of charge separation, the availability of separated charges to the substrate and the

thermodynamics of electron transfer reactions determine the efficiency of a redox reaction. The reaction of this electron –hole pair with a variety of electron acceptors and donors, as well as the electron-hole recombination processes has been well-studied [10,11]. The formation of cation radicals of organic substrates, following an electron transfer from it to the excited semiconductor has been unambiguously characterized, both from product analysis[12] as well as by spectroscopic studies [13]. Of the two possible pathways for the initial oxidation reactions namely, the one involving direct oxidation of organic substrate and other proceeding through $OH^{\bullet}$ radical mediated reactions, the current prevailing view favors the latter. However, it is also possible that the nature of the primary process may vary with the nature of the molecule. Organic molecules, which can adhere strongly to the surface of the semiconductors, for example, will be more susceptible to direct oxidation.

The adsorption properties of an organic substrate and its subsequent reactive intermediates and products on the semiconductor surface are also key issues for a synthetically useful redox transformation or degradation.

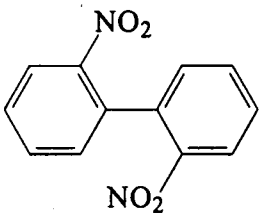
It may be used as an alternative method for selective organic synthesis under environmentally benign conditions and aid the pollution reduction by eliminating potential wastes at their source. Such heterogeneous photocatalysis has been carried out both in

organic solvents (usually acetonitrile)[14-20] and in aqueous suspensions[21-30] and also in acetonitrile/water mixture [31].

Since the chemistry of such processes is complex, careful analytical monitoring using different techniques is essential in order to control all transformation steps, to identify harmful intermediate, to understand and interpret the reaction mechanism. The assessment of pollutant disappearance in the early steps is not sufficient to ensure the absence of residual products because the heterogeneous treatment may give rise to variety of organic intermediates which can themselves be toxic, and in some cases, more persistent than the original substrate.

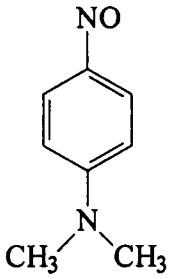
We, therefore, chose to study the photocatalysed reactions of few selected priority organic pollutants such as 2, 2′- dinitrobiphenyl (**1**), N,N-dimethyl-4-nitrosoaniline (**2**), 4-(dimethylamino)benzaldehyde (**3**), Phthalaldehyde (**4**) and tetramethyl-1,4-benzoquinone (**5**) (**Shown in chart 4.1**) in acetonitrile/water mixture with an aim to identify the intermediate products formed during the photo-oxidation process in order to have a better understanding of the reaction mechanisms involved.

These model compounds, **1 - 5** are being used extensively for a variety of purposes and hence being discharged in the wastewater leading to water pollution.



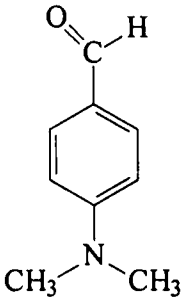
2,2'-dinitrobiphenyl

(1)



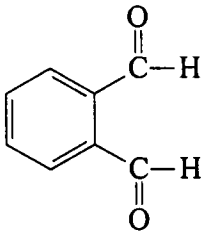
N,N-dimethyl-4-nitrosoaniline

(2)



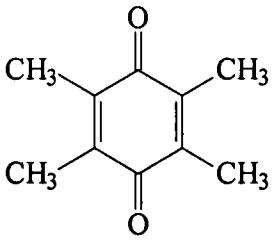
4-(Dimethylamino)benzaldehyde

(3)



Phthalaldehyde

(4)



Tetramethyl-1,4-benzoquinone

(5)

Chart 4.1: Chemical Structure and Chemical name

4.3 Experimental

4.3.1. Reagents

Analytical grade compounds, **1 – 5** were obtained from Fluka and used as such without any further purification. Reagent grade acetonitrile and double distilled water were employed to make solutions for irradiation experiments. Titanium dioxide (Degussa P25) was used as photocatalyst in this study. Degussa P25 consists of 75% anatase and 25% rutile with a specific BET-surface area of 50 m^2g^{-1} and a primary particle size of 20 nm. [32,33]

4.3.2. Procedure

The desired concentration of the compound was prepared in acetonitrile/water mixture (1:1) and taken in a photochemical reactor made of "Pyrex" glass (250 mL capacity). The required amount of photocatalyst was added and irradiated using a 250 W high pressure mercury lamp with continuous stirring and purging with molecular oxygen. The photocatalyst was removed through centrifugation from the irradiated mixture and solution was extracted with chloroform, which was subsequently dried over anhydrous sodium sulfate. The removal of the solvent under reduced pressure gave a residual mass, which was analyzed by GC/MS. For GC/MS analysis a Shimadzu gas chromatograph and mass spectrometer (GCMS-QP 5000) equipped with a 25 m CP SIL 19 CB (d = 0.25 mm) capillary column, operating temperature programmed (injection temp, Column temp, 260 °C for 25 min at the rate of 10 °C min^{-1}) in split mode, injection volume (1.0 µL)

with helium as a carrier gas was used.

4.4. Results and Discussion

4.4.1. Photolysis of TiO_2 suspensions containing 2, 2′-dinitro biphenyl (1)

A solution of 2, 2′-dinitrobiphenyl (**1**, 4 mM) in acetonitrile/water mixture (1:1, 250 mL) in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) was irradiated for 11 h under oxygen atmosphere. The catalyst was removed and the irradiated mixture was extracted with chloroform which was dried over anhydrous sodium sulfate. The removal of the solvent under reduced pressure gave a residual mass. The GC/MS analysis of the residue showed the formation of several products of which three products namely, 2-hydroxy-2′-nitrobiphenyl (**6**), 2, 2′ dihydroxy biphenyl (**7**) and 2-aminobiphenyl (**11**) appearing at retention times (t_R) 10.588, 4.593 and 7.665 min were identified along with some unchanged starting material appearing at t_R 11.653. The products were identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, which are indicated below;

Compound **6**: m/z, 215 (M^+), 198, 185, 168, 157, 141, 139, 115, 102, 89, 75, 63 and 51.

Compound **7**: m/z, 180 (M^+), 145, 120, 109, 84, 74, 61, 49 and 41.

Compound **11**: m/z, 168 (M^+), 167, 139, 115, 102, 84, 77, 63, 51 and 39.

There have been less reported investigations on reductive

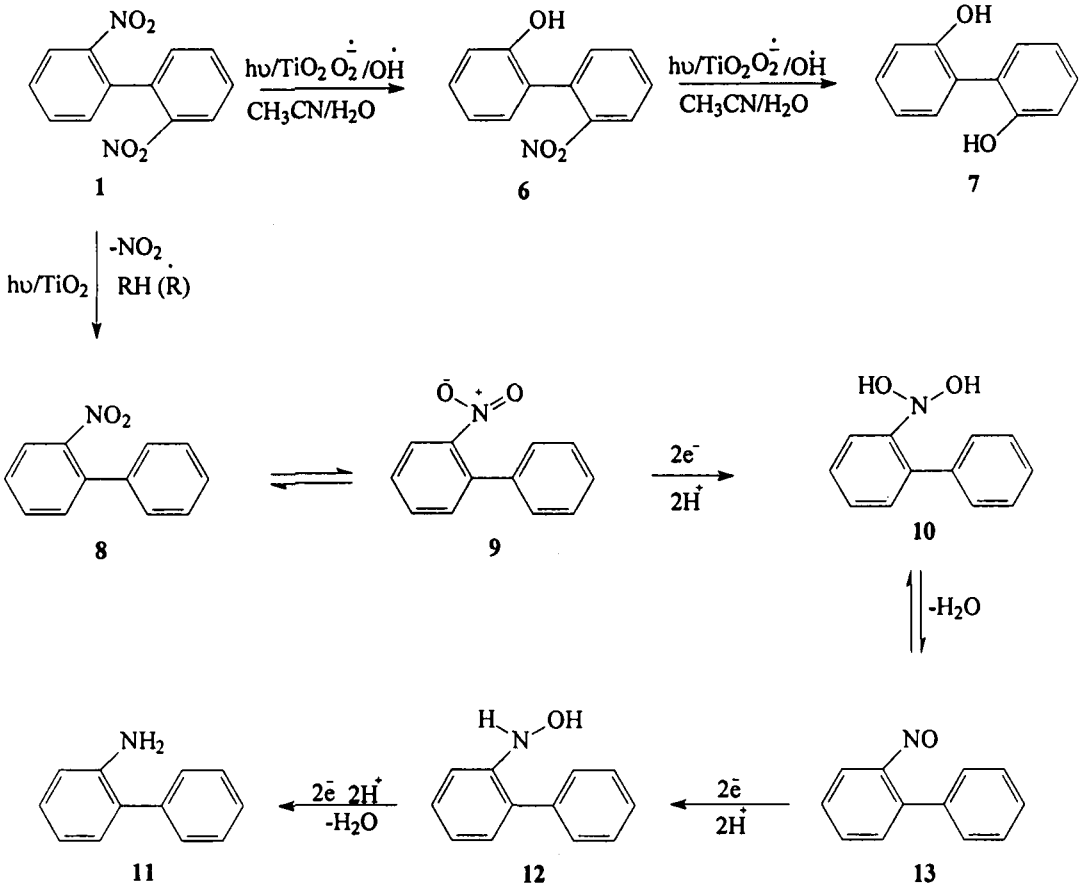
transformations of organic compounds with semiconductor particles as photocatalyst due to the fact that the reducing power of a conduction band electron for most of the semiconductors is significantly lower than the oxidizing power of a valence band electron hole. However, reductive transformations may be more suitable for organic synthesis because they are easier to control. Similar kind of reduction has been reported for many compounds[14] and also for many-substituted nitrobenzene to their corresponding amino derivatives.[34]

Here, we report the reduction of 2, 2′-dinitrobiphenyl (**1**) to 2-aminpbiphenyl (**11**) along with two other hydroxylated products **6** and **7** respectively. In this study, nitro group is reduced to give corresponding amino derivative **11**. A six-electron reduction mechanism involving two sequential steps of electron transfer, protonation and dehydration has been proposed in **Scheme 1** for the formation of products in the photocatalysis of **1** .

4.4.2. Photolysis of TiO_2 suspensions containing N, N-dimethyl-4-nitrosoaniline (2)

The irradiation of N, N-dimethyl-4-nitrosoaniline (**2**, 4 mM) in 1:1 acetonitrile/water mixture (250 mL) for 2.5 h in presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) and work up of the reaction mixture under analogous conditions followed by GC/MS analysis of the irradiated mixture showed the formation of N, N-dimethyl-4-nitroaniline (**14**) appearing at retention time (t_R) 9.263 min along with some unchanged

Scheme 1


NO2
NO2
1
hυ/TiO2 O2-/OH
CH3CN/H2O
OH
NO2
6
hυ/TiO2 O2-/OH
CH3CN/H2O
OH
HO
7
hυ/TiO2
-NO2
RH (R)
NO2
8
9
2e-
2H+
HO
N
OH
10
-H2O
NO
13
2e-
2H+
H
N
OH
12
2e- 2H+
-H2O
NH2
11

starting material appearing at t_R 8.138 min. Furthermore, prolong irradiation of the solution upto 16 h, led to the formation of an additional product namely, N, N dimethyl - 1, 4-benzenediamine (**15**) appearing at retention time (t_R) 6.107 min. Both the products were identified by comparing the molecular ion and mass fragmentation pattern (given below) with those reported in the GC/MS library.

Compound **14**: m/z, 166 (M^+), 150, 136, 119, 105, 91, 77, 63 and 42.

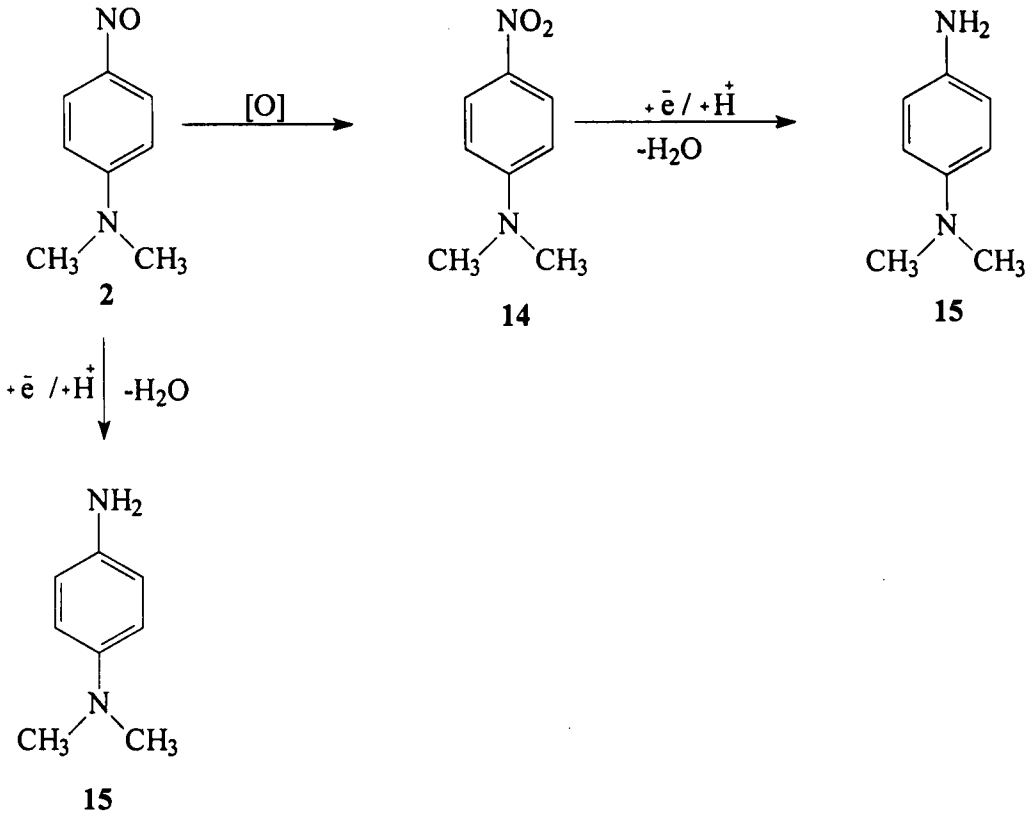
Compound **15**: m/z, 136, 121, 107, 93, 77, 65 and 39.

The parent compound **2** can either directly reduces to give corresponding amine, **15** or firstly oxidized to a nitro derivative, **14** then undergo reduction to give the observed product **15** as outlined in **Scheme 2**. A similar kind of reduction has been reported for the conversion of nitro to amino group in the case of substituted nitrobenzene derivatives[34].

4.4.3. Photolysis of TiO_2 suspensions containing 4-(dimethyl amino) benzaldehyde (3)

Photolysis of 4-(dimethylamino)benzaldehyde (**3**, 4 mM) in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) in acetonitrile/water mixture (1:1, 250 mL) for 9 h and the work up of the reaction mixture followed by GC/MS analysis of the residue led to the formation of a demethylated product **17** appearing at retention time (t_R) 7.455 min along with some unchanged starting material appearing at t_R 7.722 min. The product was characterized by comparing the molecular ion

Scheme 2



and mass fragmentation pattern with those reported in the GC/MS library, as indicated below;

Compound **17**: m/z, 134 (M^+), 118, 106, 91, 77, 65, 53 and 41.

The formation of **17** from **3** could be understood in terms of pathway shown in **scheme 3**. The model compound **3** on irradiated TiO_2 may undergo transfer of an electron followed by loss of methyl radical to give anionic species **16** which may abstract a proton to give the observed product,**17** .

4.4.4. Photolysis of TiO_2 suspensions containing Phthalaldehyde (4)

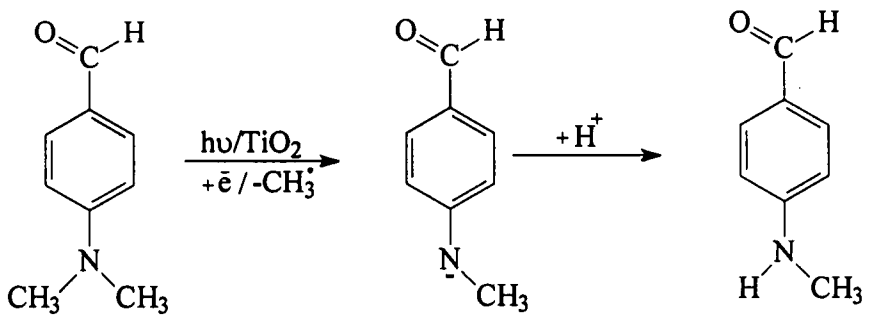
The irradiation of phthalaldehyde (**4**, 4 mM) in acetonitrile/water mixture (1:1, 250 mL) for 1 h in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) and work up of the reaction mixture under analogous conditions followed by GC/MS analysis of the organic extract showed the formation of 1(3H)-isobenzofuranone (**23**) appearing at retention time (t_R) 5.933 min. Furthermore, when the irradiation was continued upto 8 h, it lead to the formation of an additional product 2-formyl-benzoic acid (**20**) appearing at retention time (t_R) 7.240 min. The products were identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, as indicated below;

Compound **23**: m/z, 134 (M^+), 105, 89, 77, 63, 51 and 41.

Compound **20**: m/z, 149 (M^+), 133, 122, 105, 93, 77, 65, 50 and 39.

The formation of products **20** and **23** from **4** involving electron

Scheme 3



3 **16** **17**

transfer reactions, reaction with hydroxyl radicals and superoxide radical anions formed during the photo-oxidation process could be understood in terms of the pathways shown in **Scheme 4**.

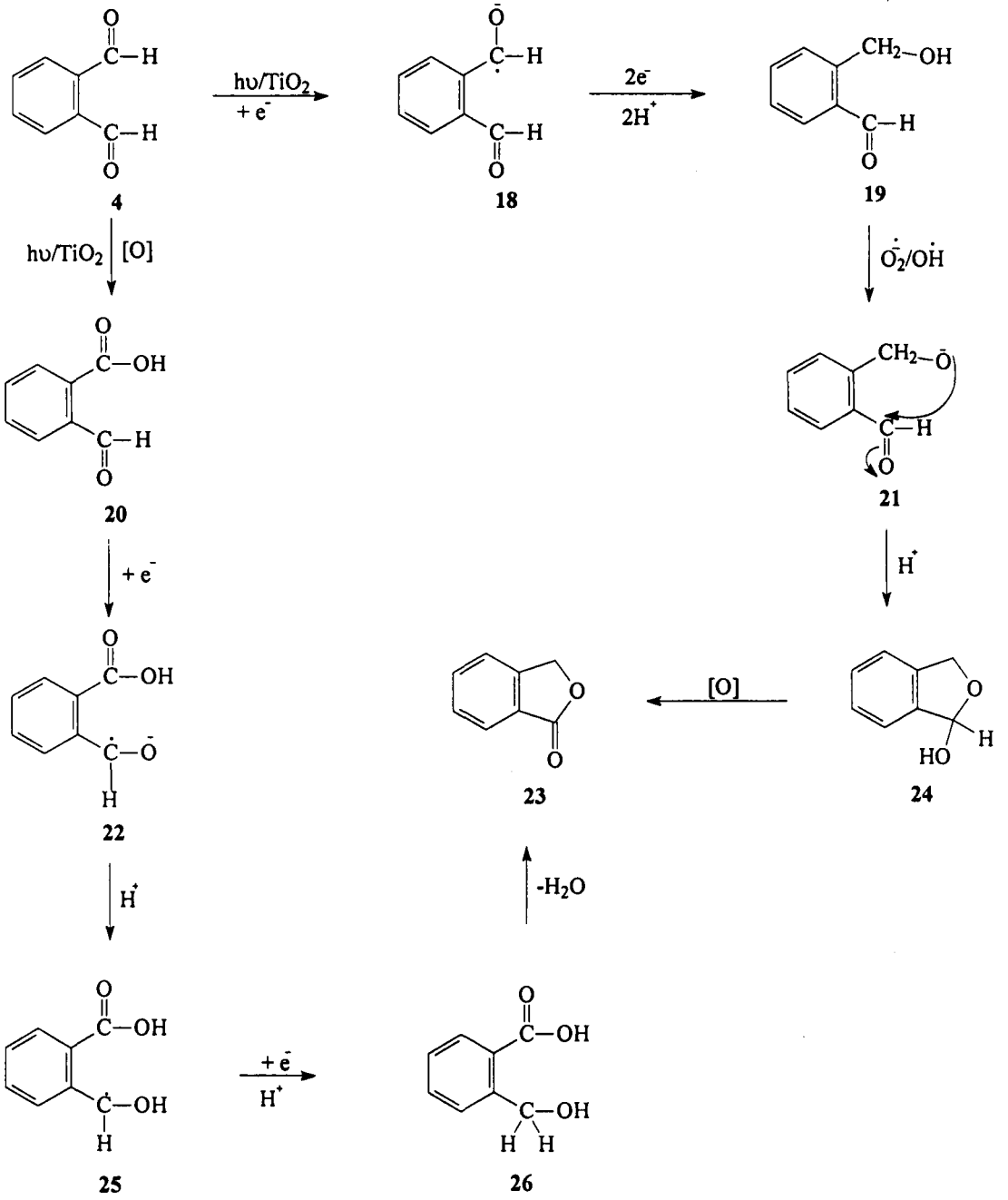
The model compound **4** upon the transfer of an electron can form the radical anion species **18** which may either undergo transfer of one more electron to give dianion followed by abstraction of two protons or may undergo abstraction of a proton and a hydrogen atom to give **19**. This species in the presence of hydroxyl radical or superoxide radical anion can generate **21** which may undergo cyclisation followed by oxidation to give the observed product **23**.

The starting compound, **4** on irradiated TiO_2 may undergo oxidation to give the observed product **20** which may also undergo addition of electron followed by cyclisation to give the observed product **23** as an alternative route for the formation of this product.

4.4.5. Photolysis of TiO_2 suspensions containing tetramethyl-1, 4-benzoquinone (5)

The photolysis of tetramethyl-1, 4-benzoquinone (**5**, 4 mM) in 1:1 acetonitrile/water mixture (250 mL) in the presence of TiO_2 (Degussa P25, 1.5 gL^{-1}) for 16 h and workup mixture of the reaction mixture under analogous conditions gave a residual mass. The GC/MS analysis of the residue gave a mixture of tetramethyl hydroquinone (**34**) and 2,5-furandione- 3,4-dimethyl- (**33**) appearing at retention time (t_R) 6.575 and 3.187 min respectively alongwith some unchanged starting material appearing at t_R 5.862 min. The products were

Scheme 4



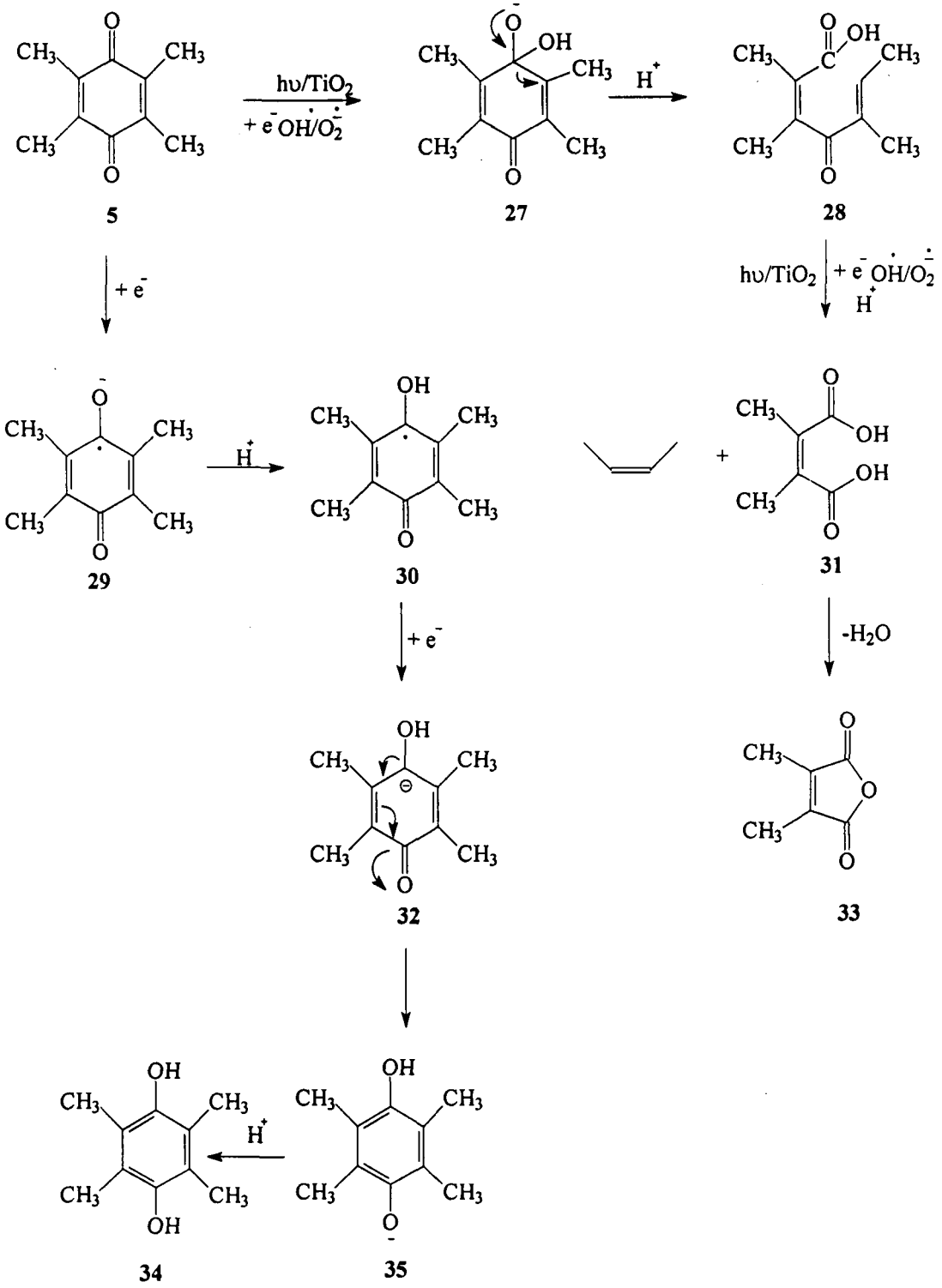
identified by comparing the molecular ion and mass fragmentation pattern (indicated below) with those reported in the GC/MS library.

Compound **34**: m/z, 166 (M^+), 151, 138, 124, 109, 95, 83, 69, 43 and 41.

Compound **33**: m/z, 126 (M^+), 125, 84, 82, 67, 54 and 41.

The parent compound **5** may accept an electron to give a hydroxyl added anionic species **27** either by the attack of hydroxyl radical or by superoxide radical anion. This species may undergo ring cleavage to give **28**, which may subsequently undergo similar kind of reaction to give rise to a dicarboxylated species **31**. The species **31** may finally lead to the formation of observed product **33** by the elimination of one molecule of water. The possible formation of tetramethyl hydroquinone (**34**) from **5** could be understood in terms of pathways shown in **Scheme 5** involving addition of two electrons followed by abstraction of two protons.

Scheme 5



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Conclusion:

The results of these studies indicate that TiO_2 can efficiently catalyze the degradation of variety of organic compounds in the presence of light. The results also indicate that degradation of the pollutant could be influenced by a number of parameters such as type of photocatalyst, pH, substrate and catalyst concentration and in the presence of electron acceptors beside atmospheric oxygen.

It could be demonstrated that photocatalytic properties of different TiO_2 materials may differ considerably for the degradation of different systems. The TiO_2 sample obtained from Degussa P25 was found to be more efficient photocatalyst for the degradation of all the compounds studied except for dye derivative cresol red. The TiO_2 sample such as Hombikat UV100, a high surface anatase catalyst, seems to be the best photocatalyst for the degradation of cresol red as compared with other TiO_2 powders.

Our studies on the photocatalytic degradation of organic pollutants indicate that some compounds degrade faster in acidic pH [2-(2,4,5- trichlorophenoxy)propionic acid, dichloroprop-P, 2,4,6 trichlorophenol and 4-nitroanisole] whereas other degrade faster in alkaline pH (cresol red, 4-cynophenol, 4-aminophenol and 2,4-dichloroaniline) depending on the type of chromophore present in the molecule. The electron acceptor such as $KBrO_3$ has been found to enhance the degradation of the compounds markedly.

The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The best degradation condition depends strongly on the specific kind of pollutant. The intermediate products formed during the process could also be responsible for the slow decomposition of the model pollutants. Identification of intermediate products formed during the photooxidation process using GC/MS analysis technique were useful source of information for the degradation pathways.

List of Publications

1. Photocatalysed reaction of few selected organic systems in presence of titanium dioxide,

   M. Muneer, D. Bahnemann, M. Qamar, M. A. Tariq and M. Faisal,

   Applied Catalysis A: General, 289 (**2005**) 224-230.

2. Photocatalysed degradation of two selected dyes in UV-irradiated aqueous suspensions of titania,

   M. Faisal, M. Abu Tariq and M. Muneer,

   Dyes and Pigments, (**in press**).

3. Semiconductor-mediated photocatalysed degradation of two selected azo dye derivatives, amaranth and bismarck brown in aqueous suspension,

   M. Abu Tariq, M. Faisal and M. Muneer,

   J. Hazardous Materials, B 127 (**2005**) 172-179.

4. Heterogenous photocatalysed degradation of two selected triphenylmethane dye derivatives in aqueous suspension of semiconductor,

   M. Faisal, Abu Tariq, M. Saquib and M. Muneer,

   J. Hazardous Materials, B (**Communicated**).

5. Photocatalytic degradation of two selected dye derivatives in aqueous suspension of titanium dioxide,

   M. Saquib, M. Abu Tariq, M. Faisal and M. Muneer,

   Desalination, (**Communicated**).

6. Heterogeneous photocatalysed reactions of three selected organic systems in aqueous suspension of titanium dioxide,

M. Faisal, M. Abu Tariq and M. Muneer

Research on Chemical Intermediates, (**under preparation**).

7. Titanium dioxide mediated photocatalysed degradation of two selected pesticide derivatives,

   M. Faisal, M. Abu Tariq and M. Muneer,

   Journal of Environmental Management, (**under preparation**).

Paper presented/accepted in conferences

8. Photocatalysed degradation of two selected dyes in UV-irradiated aqueous suspension of titania,

   M. Faisal, M. Abu Tariq and M. Muneer,

   National Conference on Recent Trends in Surface Chemistry (RTSC-05), on 13-14th March 2005, Department of Chemistry, Guru Jambheshwar University, Hisar-125 001, Haryana, India (**oral presentation**).

VITAE

Born on July 15th, 1980, at Aligarh, Uttar Pradesh, India, **MOHD FAISAL** completed his schooling in 1995. He obtained the degree of Bachelor of Science and Master of Science in Chemistry from Aligarh Muslim University, Aligarh in 2001 and 2003 respectively.

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